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(54)【発明の名称】　抗菌性吸水剤および抗菌性吸収性物品

(57)【要約】
【課題】　吸収性能、抗菌性能および粉体流動性に優れ、特に尿、血液、体液などを吸収する目的で使用される吸収性物品に有用な抗菌性吸水剤を得る。
【解決手段】　側鎖に酸基を有する吸水性樹脂中の酸基が下記一般式で示される第４級アンモニウム塩の形で存在する樹脂であり、第４級窒素原子の含有量が２×１０$^{-4}$～０．８質量％の吸水性樹脂からなる抗菌性吸水剤である。

$$-X^{-}\cdot\left[R_1-\underset{\displaystyle R_4}{\overset{\displaystyle R_2}{\overset{|}{\underset{|}{N}}}}-R_3\right]^{+}$$

［X^{-}は該吸水性樹脂のポリマー鎖に共有結合したアニオン基；R_1、R_2、R_3、R_4は有機基であり、これらの内の少なくとも１個は炭素数５～２０の脂肪族炭化水素基である］

【特許請求の範囲】
【請求項１】　側鎖に酸基を有し、酸基の少なくとも一部が第４級アンモニウム塩の形で存在し、第４級窒素原子の含有量が2×10^{-4}～０．８質量％である吸水性樹脂（Ａ）からなる抗菌性吸水剤。

$$-X^{-}\cdot[R_1-N(R_2)(R_3)-R_4]^{+} \quad (1)$$

［式中、X^{-}は吸水性樹脂（Ａ）中のポリマー鎖に共有結合したアニオン基であり、R_1～R_4は有機基であり、R_1～R_4から選ばれる２つの基が相互に結合して環を形成していてもよい。R_1～R_4のうち少なくとも１つは炭素数５～２０の脂肪族炭化水素基である。］
【請求項２】　吸水性樹脂（Ａ）中の第４級アンモニウム塩の形で存在する酸基が、下記一般式（１）で示される基である請求項１記載の抗菌性吸水剤。
【請求項３】　吸水性樹脂（Ａ）が、第４級アンモニウム塩の形で存在する酸基と、未中和の酸基および／またはアルカリ金属塩に中和された酸基とを側鎖に有する吸水性樹脂である請求項１または２記載の抗菌性吸水剤。
【請求項４】　生理食塩水（０．９％塩化ナトリウム水溶液）に対する吸収量が３０ｇ／ｇ以上の少なくとも１種の吸水性樹脂からなる吸水剤であり、
吸水性樹脂の少なくとも１種が側鎖に酸基を有し、
吸水剤成分中に第４級窒素原子を2×10^{-4}～０．８質量％含有し、
吸水剤にアンモニア産生菌を接種して２時間培養した後の混和平面培養法で測定した生菌株数が初期の生菌株数の１万分の１以下の抗菌作用を有し、かつ、
人尿中で１０時間保持した後の吸収量が、３０ｇ／ｇ以上であることを特徴とする抗菌性吸水剤。
【請求項５】　請求項１～４のいずれか記載の抗菌性吸水剤が、吸収性の繊維状支持体中に保持された層を有する抗菌性吸収性物品。
【発明の詳細な説明】
【０００１】
【発明の属する技術】本発明は、吸収性能、抗菌性能および粉体流動性に優れ、特に尿、血液、体液などを吸収する吸収性物品に有用な抗菌性吸水剤およびこれを用いた吸収性物品に関する。
【０００２】
【従来の技術】吸水性樹脂は、その吸収性能、保水能、ゲル化能を利用して、紙おむつ、失禁パッド、生理用ナプキン、母乳用パッド等の吸収性物品や、ペット用シート、ペット用床砂、排泄物処理剤、廃血液ゲル化剤、ドリップ吸収剤、鮮度保持剤などの各種用途で使用されている。しかしながら、従来の吸水性樹脂は尿、血液、体液などを吸収・保水する能力に優れるものの、抗菌機能は有していない。
【０００３】したがって、従来の吸水性樹脂が尿、血液、体液などの液体を吸収した場合、被吸収液に含まれる有機物が菌類や微生物などによって分解され、この分解生成物が悪臭発生や皮膚刺激、かぶれ等の原因となるという問題がある。更に空気中のバクテリア等によっても吸水ゲルが腐敗しやすく、腐敗によって悪臭を発散することがある。
【０００４】以上のことから、衛生面および安全性の観点から、吸水機能と抗菌機能の双方に優れた材料の出現が望まれてきた。特に、寝たきり老人や病人などに使用される大人用紙おむつや失禁者用パッドなどの吸収性物品では、悪臭やかぶれの問題は深刻であり、解決が望まれている。さらに使用済みの吸収性物品を廃棄する際に、病原菌などによる感染を防止する目的からも優れた抗菌機能を有する吸水性樹脂の出現が望まれている。
【０００５】上記に近い効果を発現させる方法として、
吸水性樹脂とゼオライトとの粉体同士の混合物（特開昭５７－２５８１３号公報、特開昭５９－１７９１１４号公報、特開昭５９－１８９８５４号公報）、
活性炭を吸水性樹脂でコーティングした組成物（特開昭５６－３１４２５号公報）、
吸水性樹脂とツバキ科植物から抽出された消臭成分とから成る組成物（特開昭６０－１５８８６１号公報）、
特定の殺菌剤（塩化ベンザルコニウム、グルコン酸クロルヘキシジン）を含有した吸水性樹脂組成物（特公平４－１７０５８号公報）、
燐酸塩化合物を含有した吸水性樹脂組成物（特開平５－１７９０５３号公報）、並びに、これらの吸収性物品への適用が提案されている。
【０００６】
【発明が解決しようとする課題】しかしながら、これら～の組成物は、吸収性物品に適用するには必ずしも満足のいく悪臭発生防止効果や腐敗抑制効果が得られなかったり、腐敗などにより吸収性能が低下するという問題点があった。さらに、抗菌機能または消臭機能を満足させるために、これらの機能を有する物質を吸水性樹脂に後処理する必要があるが、この後処理によって得られる組成物の粉体流動性が低下するという問題点があった。
【０００７】すなわち、吸水性樹脂とゼオライトとの混合物は、発生した悪臭はある程度吸着して消臭効果を発揮することができるものの、吸水性樹脂およびゼオライトともに抗菌機能を持たないことから、微生物や菌類による有機物の分解や腐敗を抑制し、悪臭の発生を防止

することができない。したがって、吸収性物品に適用しても有機物の分解による皮膚刺激やかぶれ等を抑えることはできなかった。また、振動や衝撃によってゼオライトが吸水性樹脂と分離することで発塵度が高くなったり、消臭機能にバラツキが見られた。

【０００８】活性炭を吸水性樹脂でコーティングした組成物や、吸水性樹脂とツバキ科植物から抽出された消臭成分とから成る組成物の場合、活性炭およびツバキ科植物から抽出された消臭成分が抗菌機能を示さないことから、上記のゼオライトの場合と同様の結果となり、微生物や菌類による有機物の腐敗を抑制することができなかった。また、のゼオライトのような吸着剤、のツバキ科植物から抽出された消臭剤を用いる場合、これらを吸水性樹脂に固定化するために、特別な操作を必要とするという問題点があった。

【０００９】塩化ベンザルコニウムやグルコン酸クロルヘキシジンを含有した吸水性樹脂組成物、あるいは燐酸塩化合物を含有した吸水性樹脂組成物は、ある程度の殺菌作用が認められるものの、殺菌効用の対象となる菌類や微生物の種類に限定があり、必ずしも満足のできるものではなかった。特に塩化ベンザルコニウムは、大腸菌やカンジダ菌に対する抗菌効果は優れるものの、アンモニア産生菌（Providentica rettgeri）に対する抗菌作用が比較的低いことから、尿中の有機物が分解することによるアンモニアの発生を完全には抑制できず、残存するアンモニアによって尿のｐＨがアルカリ性に変化し、その結果吸水性能が低下するという問題点がある。さらに、これらの抗菌剤で処理して得られる抗菌性の吸水性樹脂組成物は、抗菌剤の処理量によっては粉体流動性が低下するという問題点があった。

【００１０】

【課題を解決するための手段】本発明者らは、上記問題点に鑑みて、吸収性能および粉体流動性に優れ、特にアンモニア産生菌に対して優れた抗菌作用を発現し、尿を吸収した状態においても吸収性能の低下がなく、尿、血液、体液などを吸収する目的で使用される吸収性物品に有用な抗菌性吸水剤について鋭意検討した結果、本発明に到達した。

【００１１】すなわち本発明は、下記［１］、［２］の抗菌性吸水剤および［３］の抗菌性吸収性物品である。

［１］　側鎖に酸基を有し、酸基の少なくとも一部が第４級アンモニウム塩の形で存在し、第４級窒素原子の含有量が2×10^{-4}～０．８質量％である吸水性樹脂（Ａ）からなる抗菌性吸水剤。

［２］　生理食塩水（０．９％塩化ナトリウム水溶液）に対する吸収量が３０ｇ／ｇ以上の少なくとも１種の吸水性樹脂からなる吸水剤であり、

吸水性樹脂の少なくとも１種が側鎖に酸基を有し、

吸水剤成分中に第４級窒素原子を2×10^{-4}～０．８質量％含有し、

吸水剤にアンモニア産生菌を接種して２時間培養した後の混和平面培養法で測定した生菌株数が初期の生菌株数の１万分の１以下の抗菌作用を有し、かつ、

人尿中で１０時間保持した後の吸収量が、３０ｇ／ｇ以上であることを特徴とする抗菌性吸水剤。

［３］　上記［１］または［２］項記載の抗菌性吸水剤が吸収性の繊維状支持体中に保持された層を有する抗菌性吸収性物品。

【００１２】

【発明の実施の形態】本発明の抗菌性吸水剤［１］において、吸水性樹脂（Ａ）は、側鎖に酸基を有し、酸基の少なくとも一部が第４級アンモニウム塩の形で存在する。従って、吸水性樹脂（Ａ）は、吸水性樹脂の有する吸水性能と、第４級アンモニウム塩の形で存在する酸基の作用による抗菌性能とが兼備された樹脂である。

【００１３】この吸水性樹脂（Ａ）中の第４級アンモニウム塩の形で存在する酸基の抗菌性能の観点で好適な例としては、下記の一般式（１）で示される基が挙げられる。

［式中、X^-は吸水性樹脂（Ａ）中のポリマー鎖に共有結合したアニオン基であり、R_1～R_4は有機基であり、R_1～R_4から選ばれる２つの基が相互に結合して環を形成していてもよい。R_1～R_4のうち少なくとも１つは炭素数５～２０の脂肪族炭化水素基である。］

【００１４】すなわち、該吸水性樹脂（Ａ）中のポリマー鎖に共有結合した酸基の少なくとも１つが、第４級アンモニウムカチオンの対アニオン基X^-となって塩を形成した構造である。X^-としては、ポリマー鎖に共有結合したアニオン基であればよく、特に制限はないが、カルボキシルアニオン基－COO^-、スルホン酸アニオン基－SO_3^-、硫酸アニオン基、燐酸アニオン基等が挙げられ、好ましいものはカルボキシルアニオン基及びスルホン酸アニオン基、特にカルボキシルアニオン基である。R_1、R_2、R_3、R_4は、抗菌性能の観点で、好ましくは炭化水素基、より好ましくは脂肪族炭化水素基、特にアルキル基であり、且つ、少なくとも１つは炭素数５～２０のアルキル基であることが好ましい。

【００１５】吸水性樹脂（Ａ）は、第４級窒素原子の含有量が通常2×10^{-4}～０．８質量％となる範囲で、酸

基の少なくとも一部が第４級アンモニウム塩の形で存在している。該吸水性樹脂（Ａ）中の第４級アンモニウム塩の形の酸基の含有量は、該樹脂の質量に対する第４級窒素原子の含有量に換算して、通常２×１０^{-4}～０．８質量％、好ましくは１×１０^{-3}～０．４質量％、特に２×１０^{-3}～０．１質量％である。

【００１６】第４級アンモニウム塩の形ではない残りの酸基は、通常、未中和の酸基および／またはアルカリ金属塩、アンモニウム塩もしくはアミン塩に中和された酸基である。該吸水性樹脂（Ａ）中の酸基としては、カルボキシル基、スルホン酸基、硫酸基、リン酸基およびこれらの塩から選ばれる１種以上が挙げられ、上記のようにこれらが未中和のままのもの、アルカリ金属塩などとして中和されたもの、第４級アンモニウム塩の形で存在しているものが側鎖として混在している。

【００１７】該吸水性樹脂（Ａ）は、カルボキシル基および／またはアルカリ金属塩、アンモニウム塩又はアミン塩に中和されたカルボキシル基を側鎖として有するもの、特にカルボキシル基および／またはアルカリ金属塩に中和されたカルボキシル基を側鎖として有するものが好ましい。第４級アンモニウム塩の形で存在する酸基を除いて残存する中和ないし未中和のカルボキシル基は、臭気成分の一種であるアンモニアなどを吸着するという付随効果が得られる。

【００１８】（Ａ）の形状は吸水性能の観点から粉末状が好ましく、例えば、粒状、顆粒状、造粒状、リン片状、塊状、パール状、微粉末状などのいずれの形状であってもよいが、特に好ましくは、粒状、顆粒状、造粒状、リン片状および塊状である。粒度あるいは粒度分布についても特に限定はないが、好ましくは９０重量％以上が１ｍｍ以下であり、更に好ましくは９０重量％以上が０．１～０．９ｍｍ、特に９５重量％以上が０．１～０．９ｍｍである。

【００１９】（Ａ）の生理食塩水（０．９％の塩化ナトリウム水溶液）に対する吸収能は、好ましくは３０ｇ／ｇ以上、更に好ましくは３５～８０ｇ／ｇ、特に４０～７５ｇ／ｇである。なお、吸収能は後述する方法で測定される。

【００２０】吸水性樹脂（Ａ）は、例えば、側鎖に酸基を有する吸水性樹脂（ａ）の酸基の少なくとも一部を第４級アンモニウム塩の形とする操作により得られる。吸水性樹脂（Ａ）の好適な製法を例示すると、側鎖に酸基を有する吸水性樹脂（ａ）と、第４級アンモニウム炭酸塩（ｂ）とを水の存在下で反応させることにより、吸水性樹脂（Ａ）が得られる。

【００２１】この反応は、（ｂ）を構成する炭酸アニオンと、（ａ）中の酸基の少なくとも１つとがアニオン交換する、即ち、（ａ）のアニオンが、（ｂ）の第４級アンモニウムカチオンの対アニオンとなる反応により進行し、炭酸アニオンは反応により炭酸ガスとなって気化するため、副成物の残存がなく、純度の高い第４級アンモニウム塩基含有吸水性樹脂が得られる利点がある。なお、上記の反応は必ずしも１００％反応させるという意味ではなく、未反応の（ｂ）がある程度（Ａ）に残存していてもよい。すなわち、第４級アンモニウムカチオンとして塩を形成した状態と第４級アンモニウム炭酸塩の状態とが共存していても良い。また、（ａ）の酸基と反応し得る官能基を２個以上有する架橋剤を共存させて、（ａ）と（ｂ）との反応と同時に架橋構造を導入することもできる。

【００２２】吸水性樹脂（Ａ）の製造に使用できる上記吸水性樹脂（ａ）としては、側鎖に未中和の酸基および／またはアルカリ金属塩、アンモニウム塩又はアミン塩に中和された酸基を有するものが好適に使用され、吸水性樹脂（ａ）中の酸基の中和度は、好ましくは５０～８０当量％、特に６０～７５当量％である。ここで当量％の値は、酸基のうちの中和された基の％をいう。側鎖に酸基を有する吸水性樹脂（ａ）としては、その構成単位にカルボキシル基、スルフォン酸基、硫酸基、リン酸基などの未中和の酸基および／またはこれらがアルカリ金属塩、アンモニウム塩又はアミン塩として中和された基を側鎖に有する吸水性樹脂であれば種類および製造方法は特に限定されない。通常、（ａ）中の中和されていない酸基が、第４級アンモニウム炭酸塩（ｂ）との反応にあずかる。

【００２３】吸水性樹脂（ａ）の好適な例としては、カルボキシル基および／またはその塩を有する吸水性樹脂（ａ１）、スルホン酸基および／またはその塩を有する吸水性樹脂（ａ２）、リン酸基および／またはその塩を有する吸水性樹脂（ａ３）などが挙げられ、これらの具体例は以下の通りである。カルボキシル基および／またはその塩を有する吸水性樹脂（ａ１）の例としては、

・特公昭５３－４６１９９号、特公昭５３－４６２００号各公報などに記載のデンプン－アクリル酸（塩）共重合体の架橋物、

・特公昭５４－３０７１０号、特開昭５６－２６９０９号各公報などに記載の逆相懸濁重合法による架橋あるいは自己架橋されたポリアクリル酸塩、

・特開昭５５－１３３４１３号公報などに記載の水溶液重合（断熱重合、加圧重合、薄膜重合、噴霧重合など）により得られる架橋ポリアクリル酸（塩）、

・特開昭５２－１４６８９号、特開昭５２－２７４５５号各公報などに記載のビニルエステルと不飽和カルボン酸またはその誘導体との共重合体ケン化物、

・イソブチレン－無水マレイン酸共重合体架橋物、デンプン－アクリロニトリル共重合体の加水分解物、架橋カルボキシメチルセルロース誘導体、アクリル酸（塩）とアクリルアミドとの共重合体架橋物、アクリルアミド重合体架橋物あるいはその部分加水分解物などが挙げられる。上記吸水性樹脂（ａ１）は２種以上併用してもよ

い。また、上記吸水性樹脂（ａ１）の粉末の表面近傍を更に表面架橋せしめた表面架橋型吸水性樹脂も本発明に好適に使用できる。表面架橋の方法（表面架橋剤の種類と添加量、架橋させる条件など）は公知の方法が適用できる。

【００２４】スルフォン酸基および／またはその塩を有する吸水性樹脂（ａ２）の具体例としては、特開昭５８－２３１２号、特開昭６１－３６３０９号各公報などに記載のスルホン酸基含有モノマーを共重合した架橋ポリアクリル酸（塩）などが挙げられる。このような吸水性樹脂中のカルボキシル基の一部をスルフォン酸基に置換した吸水性樹脂に使用されるスルフォン酸基を有する単量体の例としては、脂肪族または芳香族ビニルスフォン酸［ビニルベンゼンスルフォン酸、アリルスルフォン酸、ビニルトルエンスルフォン酸、スチレンスルフォン酸など］、（メタ）アクリルスルフォン酸［（メタ）アクリル酸スルホエチル、（メタ）アクリル酸スルホプロピルなど］、（メタ）アクリルアミドスルフォン酸［２－アクリルアミド－２－メチルプロパンスルフォン酸］などが挙げられる。

【００２５】リン酸基および／またはその塩を有する吸水性樹脂（ａ３）の具体例としては、前述の架橋ポリアクリル酸（塩）中のカルボキシル基の一部をリン酸基を有する単量体に置換した吸水性樹脂が挙げられる。リン酸基を有する単量体の具体例としては、メタクリロイドキシエチルフォスフェート、アクリロイドキシエチルフォスフェートなどが挙げられる。

【００２６】（ａ１）～（ａ３）のうち好ましいものは、カルボキシル基および／またはその塩を有する吸水性樹脂（ａ１）であり、更に好ましいものは、比較的大きな吸収能力を発揮し、第４級アンモニウム塩を形成させる際に反応性が優れるという点で、アクリル酸およびアクリル酸塩を主構成単位とする水不溶性の吸水性樹脂である。なお、該吸水性樹脂（ａ）中の酸基を中和した塩とは、通常ナトリウム塩、カリウム塩等のアルカリ金属塩であるが、用途によってはアンモニウム塩、アミン塩などの有機塩であってもよい。

【００２７】カルボキシル基および／またはその塩を有する吸水性樹脂（ａ１）において、カルボキシル基の中和度は、前記のとおり、好ましくは５０～８０％、特に６０～７５％である。吸水性樹脂（ａ１）を用いれば、誘導される吸水性樹脂（Ａ）がカルボキシル基を有することにより、前述のとおり、カルボキシル基が第４級アンモニウム塩の形で存在する部分を除いて残存するカルボキシル基が臭気成分の一種であるアンモニアなどを吸着するという付随効果が得られる。カルボキシル基の中和度が５０％未満の場合、吸収性能が低下してくると共に、得られる抗菌性吸水剤のｐＨが酸性となり、皮膚に対する安全性の面でも好ましくない。カルボキシル基中和度が８０％を越える場合、アンモニアなどを吸着する効果が乏しくなるとともに、得られる抗菌性吸水剤のｐＨがアルカリ性となり、この場合も皮膚に対する安全性の面で好ましくない。

【００２８】吸水性樹脂（Ａ）の製造に使用できる上記第４級アンモニウム炭酸塩（ｂ）の例としては下記一般式（２）または（３）で示される化合物が挙げられる。

【００２９】

$$[R_1-\overset{\displaystyle R_2}{\overset{|}{N^+}}-R_3]\cdot R_5CO_3^- \qquad (3)$$
$$\qquad\quad |$$
$$\qquad\quad R_4$$

［各式中、R_1～R_4は有機基、R_5は低級アルキル基であり、R_1～R_4から選ばれる２つの基が相互に結合して環を形成していてもよい。］

【００３０】（ｂ）が一般式（２）の化合物の場合は、（ａ）との反応により炭酸ガスと共に低級アルコール類も生成するが、水に溶解するか気化するため、やはり副成物の残存がなく純度の高い樹脂（Ａ）が得られる。一般式（２）または（３）で示される化合物は例えば、炭素数５～２０の脂肪族アルキル基を少なくとも１個有する３級アミン（ｂ１）と炭酸ジエステル（ｂ２）の反応により合成することができる。

【００３１】（ｂ１）としてはオクチルジメチルアミン、デシルジメチルアミン、ラウリルジメチルアミン、ミリセチルジメチルアミン、セチルジメチルアミン、ステアリルジメチルアミン、ジヘキシルメチルアミン、ジオクチルメチルアミン、ジデシルメチルアミン、ジドデシルメチルアミン、２－ヘプタデセニル－ヒドロキシエチルイミダゾリンなどが挙げられる。好ましいものは炭素数５～２０の脂肪族アルキル基を２個有する３級アミンであり、更に好ましいものはジオクチルメチルアミンおよびジデシルメチルアミンである。（ｂ２）としては炭酸ジメチル、炭酸ジエチル、炭酸エチルメチル、炭酸

ジプロピルなどが挙げられるが、アルキル基の炭素数の少ない炭酸ジメチルが反応性に優れるので好ましい。

【００３２】第４級アンモニウム炭酸塩（ｂ）の製造時における３級アミン（ｂ１）と炭酸ジエステル（ｂ２）とのモル比は、通常１：（０．３～４．０）、好ましくは１：（０．５～２．５）であり、反応温度は通常３０～１５０℃、好ましくは５０～１２０℃である。必要によりメタノールやエタノールのような溶媒、あるいはこれらと水との混合溶媒が使用できる。

【００３３】該吸水性樹脂（Ａ）を製造する際の吸水性樹脂（ａ）と第４級アンモニウム炭酸塩（ｂ）との比率は、（Ａ）の中の第４級窒素原子の含有量が、前記範囲内となるような比率とすればよく、目的とする吸収性能と抗菌性能とのバランスによって種々変化させることができる。通常（ａ）：（ｂ）の比率は、（ａ）中の酸基と（ｂ）の当量比で１：（３×１０$^{-5}$～０．３）、好ましくは１：（１×１０$^{-4}$～０．１）、さらに好ましくは１：（３×１０$^{-4}$～８×１０$^{-2}$）である。（ｂ）の当量比が３×１０$^{-5}$未満では、得られる組成物の抗菌効果が乏しくなる。一方（ｂ）の当量比が０．３で十分な抗菌効果を発揮するため、これ以上比率を高めても抗菌効果は殆ど増加しないことから不必要である。

【００３４】酸基を有する吸水性樹脂（ａ）と第４級アンモニウム炭酸塩化合物（ｂ）とを水の存在下で反応させて該吸水性樹脂（Ａ）を得る更に具体的な方法としては、例えば、下記（１）～（４）の方法が挙げられ、（１）および（４）の方法が好ましい。

（１）吸水性樹脂（ａ）の粉末に第４級アンモニウム炭酸塩（ｂ）の水性液を混合した後、反応させて、吸水性樹脂の粉末の表面近傍に第４級アンモニウム塩を形成させる方法。

（２）（ａ）の製造工程で得られる含水ゲル状重合体に（ｂ）を混練した後、加熱して反応および乾燥させて粉砕する方法。

（３）（ａ）に水を吸収させて吸水ゲルを作成した後、（ｂ）をで混練し、加熱して反応および乾燥させて粉砕する方法。

（４）（ａ）に（ｂ）の水溶液を吸収させて含水ゲルを作成し、混練した後、加熱して反応および乾燥させて粉砕する方法が挙げられる。

【００３５】（１）～（４）の方法において用いる水の量は、通常（ａ）１００質量部に対して１～５００質量部、好ましくは５～４５０質量部である。水の量が１質量部未満では（ａ）と（ｂ）との反応が十分に進行せず、一方、５００質量部を越えると、（ａ）と（ｂ）との反応には支障はないが、その後に多量の水を蒸発させねばならず経済的でない。

【００３６】上記（１）～（４）の方法において、（ａ）と（ｂ）とを混合する工業的な装置については特に限定はなく、従来から公知の装置が使用できる。例えば（ａ）の粉末と（ｂ）の水溶液を混合する工業的な装置としては、万能混合機、タービュライザー、ナウター型混合機、リボンブレンダー、コニカルブレンダー、Ｖ型混合機、スクリュー式混合機、流動層式混合機、スプレー混合機、モルタルモキサーなどが挙げられる。

（ａ）の含水ゲルまたは吸水ゲルに（ｂ）を混練する工業的な装置としては、例えば、ニーダー、一軸あるいは双軸の押し出し混合機、万能混合機、ギアコンパウンダー、ミンチ機、ナウター型混合機およびスクリュー型混合機などが挙げられる。

【００３７】（ａ）と（ｂ）とを反応させる温度については特に限定はないが、下記との方法が例示できる。

上記（１）の方法のように、反応させる際の（ａ）が粉末状の場合は、好ましくは１～１５０℃、特に１０～１３０℃である。

上記（２）～（４）の方法のように、反応させる際の（ａ）が含水ゲル状であり反応と共に乾燥が必要な場合は、好ましくは４０～１５０℃、特に４０～１３０℃である。必要により減圧下で反応および乾燥を行わせることもできる。温度が０℃以下では水の凝固が起こり好ましくなく、一方、１５０℃を越えると（ｂ）の種類によっては分解を生じることがあり、好ましくない。

【００３８】本発明の吸水剤［１］は、該吸水性樹脂（Ａ）と共に、第４級アンモニウム基を有しない通常の吸水性樹脂（Ａ’）を含有するものであってもよく、但しこの場合は、均一な抗菌性能が発揮されるよう両者は均一に混合されていることが好ましい。またこの場合は、抗菌性能の観点から、吸水性樹脂（Ａ）、（Ａ’）の合計質量中の（Ａ）が有する第４級窒素原子の含有量を２×１０$^{-4}$質量％以上とする必要があり、この量は、好ましくは１×１０$^{-3}$質量％以上、特に２×１０$^{-3}$質量％以上である。

【００３９】吸水性樹脂（Ａ’）の生理食塩水に対する吸収能の好ましい範囲は、吸水性樹脂（Ａ）と同様であり、樹脂の種類についても特に限定はない。この吸水性樹脂（Ａ’）の代表例が、前記に例示した側鎖に酸基を有する吸水性樹脂（ａ）であり、（ａ）中の好ましいものや、中和度も前記と同様である。又、吸水性樹脂（Ａ’）の形状や粒度、粒度分布の範囲は、吸水性樹脂（Ａ）と同様である。

【００４０】本発明の吸水剤［２］は、生理食塩水（０．９％塩化ナトリウム水溶液）に対する吸収量が３０ｇ／ｇ以上の少なくとも１種の吸水性樹脂からなり、この吸水性樹脂の少なくとも１種は側鎖に酸基を有する。また、吸水剤［２］の成分中に第４級窒素原子を２×１０$^{-4}$～０．８質量％含有することを特徴とする。

【００４１】本発明の吸水剤［２］は、塩化ベンザルコニウムを使用する公知の抗菌性吸水性樹脂組成物（例えば特公平４－１７０５８号公報に記載の組成物）と比較

して、大腸菌に対する抗菌作用だけでなく、アンモニア産生菌に対する抗菌作用にも優れている。即ち、アンモニア産生菌を接種して２時間培養した後に混和平面培養法で測定した生菌株数は、初期の生菌株数の１万分の１以下に低減され、アンモニアの発生を防止できるという優れた作用を有する。なお、抗菌効果およびアンモニア発生量の評価は後述する方法で測定される。

【００４２】本発明の吸水剤［２］の、人尿中で１０時間保持した後の吸収量は、通常３０ｇ／ｇ以上、好ましくは３５～８０ｇ／ｇ、特に４０～７５ｇ／ｇである。なお人尿中で１０時間保持した後の吸収量は後述する方法で測定される。

【００４３】上記ような構成と吸水性能および抗菌性能における特徴を有する本発明の吸水剤［２］の実施態様例としては、以下のものが例示される。

（１）前記吸水性樹脂（Ａ）［生理食塩水に対する吸収量が３０ｇ／ｇ以上のものを選択］からなる吸水剤。

（２）（Ａ）と前記吸水性樹脂（Ａ’）の均一な混合物［第４級窒素原子が2×10^{-4}～０．８質量％となる混合比。（Ａ）および（Ａ’）は生理食塩水に対する吸収量が３０ｇ／ｇ以上のものを選択］

（３）（Ａ）［生理食塩水に対する吸収量が３０ｇ／ｇ以上のものを選択］と前記第４級アンモニウム炭酸塩（ｂ）［前記R_1、R_2、R_3、R_4の有機基を有するもの］との均一な混合物。

（４）（Ａ）と（Ａ’）と（ｂ）との均一な混合物［第４級窒素原子が2×10^{-4}～０．８質量％となる混合比。（Ａ）、（Ａ’）、（ｂ）は（２）、（３）項と同様のもの］

【００４４】本発明の吸水剤［１］、［２］は、その吸水性能、抗菌性能などの作用効果を損なわない範囲で、必要により吸水性樹脂と共に、任意の工程で増量剤、添加剤として有機質粉体（例えばパルプ粉末、セルロース誘導体、天然多糖類など）、無機物質（二酸化ケイ素、酸化アルミニウム、酸化マグネシウム、ケイ酸アルミニウム、ケイ酸ナトリウム、ケイ酸マグネシウムなど）、酸化防止剤、還元剤、キレート化剤、界面活性剤、消臭剤、着色剤、香料などを配合したものとすることができる。これらの量は、吸水性樹脂の質量に対して通常１０質量％以下、好ましくは５質量％以下である。

【００４５】本発明の吸水剤［１］および／または［２］を各種の吸収性物品に適用することにより、吸水効果と抗菌効果の双方に優れた吸収性物品が得られる。吸収性物品に吸水剤［１］および／または［２］を適用する方法としては、吸水剤［１］および／または［２］が吸水性の支持体中に保持された層を形成しておればよく、例えば、層状に配置されたパルプ、熱融着性繊維あるいはこれらの混合物などの繊維状物の層の間に散粒する方法、パルプおよび／または熱融着性繊維などの繊維状物と混合する方法、二枚以上の吸水紙や不織布でサンドイッチする方法などが挙げられる。

【００４６】本発明の吸水剤［１］および／または［２］は粉体流動性が良好で、従来の吸水性樹脂と同様のハンドリング適性を有していることから、従来から公知の設備で吸収性物品を製造することができる。吸収性物品への抗菌性吸水剤の添加量は、吸収性物品の種類やサイズ、目標とする吸収性能に応じて種々変化させることができる。例えば、吸収性物品が紙おむつ、失禁パッド、手術用アンダーパッド、産褥用マットなどの場合、通常３～２０ｇ／枚の添加量であり、吸収性物品が生理用ナプキン、パンティーライナー、母乳パッド、創傷面保護用ドレッシング材などの場合、通常０．２～３ｇ／個である。二枚以上の吸水紙や不織布でサンドイッチしたシート状物に適用する場合、通常１０～８０ｇ／m^2程度が適当である。

【００４７】

【実施例】以下、実施例および比較例により本発明をさらに説明するが、本発明はこれらに限定されない。抗菌性吸水剤そのものの吸収量、抗菌効果および抗菌性吸水剤を使用した吸収性物品の効果確認テストは下記の方法により測定した。以下特に定めない限り、％は質量％を示す。

【００４８】（１）吸収量：２５０メッシュのナイロンネット製ティーバッグに試料１．０ｇを入れ、これを過剰の生理食塩水（０．９０％食塩水）中に１時間浸して吸収させた後、引き上げて垂直に吊すことによって１５分間水切りを行い、増加重量を測定する。この増加重量を吸収量とした。

【００４９】（２）粉体流動性：粉体流動性の評価は安息角を測定した。安息角の測定はパウダーテスター（ホソカワミクロン株式会社製）を使用し、試料を篩い（目開き７１０μｍ）中に適当量を静かに入れた後、振動・タッピングをしながら篩いの下にセットした付属のガラス製ロートの先端から付属の円盤の上に流出させる。堆積した粉体の稜線が一定の角度になったら試料の流出を止めて、堆積した粉体の稜線に分度器の直線部が平行になるように分度器を動かし安息角を求めた。安息角が大きいほど粉体流動性に劣ることを表す。

【００５０】（３）抗菌性吸水剤の抗菌性テスト：３００ｃｃフラスコに感受性ブイヨン培地３．４５ｇと水１５０ｍｌを入れ溶解した後、オートクレーブ滅菌する。この培地に試験試料１．０ｇを添加して撹拌しながら膨潤させた後、初期の菌株数が1×10^6個／ｍｌとなるように大腸菌（菌番号：ＪＣＭ１６４９）を接種した。このサンプルを３７℃で振とう培養して、２時間後および１０時間後にサンプリングし、必要に応じて滅菌生食水にて段階希釈を行う。このサンプリング品または希釈品を滅菌シャーレに１ｍｌずつ入れた後、寒天培地を２０ｍｌ注ぎ、シャーレ上に均一に分散固化させ、３７℃で２日間培養する。培養後にコロニーカウントし、希釈

倍率をかけて生菌株数とする。なお、生菌株数測定は、混和平面培養法にて行う。一方、ブランクとして試料を添加せず、大腸菌のみを接種した場合の生菌株数は、２時間後で5×10^{8}個／ｍｌ、１０時間後で6×10^{9}個／ｍｌであった。同様にしてアンモニア産生菌についても抗菌性をテストした。この場合、初期の菌株数が1×10^{7}個／ｍｌとなるようにアンモニア産生菌（Providentica rettgeri；菌番号：ＩＦＯ１３５０１）を接種した。一方、ブランクとして試料を添加せず、アンモニア産生菌のみを接種した場合の生菌株数は、２時間後で8×10^{7}個／ｍｌ、１０時間後で4×10^{9}個／ｍｌであった。

【００５１】（４）人尿中で１０時間保持した後の吸収量：３００ｍｌのビーカーに新鮮人尿（５名の人尿を混ぜ合わせた尿）１５０ｍｌと前述のアンモニア産生菌を添加して混合し、液温を３７℃に調整する。２５０メッシュのナイロンネット製ティーバッグに試料１．０ｇを入れ、これを上記の液中に１０時間浸して吸収、保存した後、引き上げて垂直に吊すことによって１５分間水切りを行い、増加重量を測定する。この増加重量を人尿中で１０時間保持した後の吸収量とした。

【００５２】（５）抗菌性吸水剤を適用した吸収性物品の効果確認テスト：

・吸収性物品の作成：１４ｃｍ×３５ｃｍの長方形に裁断したポリエチレンシートに、同じ大きさのティシュペーパーと坪量１００ｇ／m^2のフラッフパルプ層を重ねる。次いで試料２．９４ｇをフラッフパルプ上に均一に散布し、更に坪量１００ｇ／m^2のフラッフパルプ層とティッシュペーパーおよび不織布をこの順で重ねる。この積層物を５ｋｇ／cm^2の圧力で９０秒間プレスすることによりモデル紙おむつを作成する。

・悪臭防止効果テスト：抗菌性吸水剤を適用したモデル紙おむつの中央部に新鮮尿８０ｍｌを加えて吸収させ、５リットルの広口瓶に入れて密閉する。これを４０℃に設定した恒温槽内で１０時間保管する。その後、無臭室内で広口瓶の蓋を開けて臭いを嗅ぎ、次の６段階で臭気強度を評価する。評価はＴ＆Ｔオルファクトメーター法にて臭気判定能力確認済みの１０人のパネラーで実施し、平均値を求める。

【００５３】

０：無臭

１：やっと感知できる臭い（感知イキ値濃度）

２：何の臭いかわかる弱い臭い（認知イキ値濃度）

３：楽に感知できる臭い

４：強い臭い

５：強烈な臭い

【００５４】（６）吸収性物品の性能テスト：

・吸収量：モデル紙おむつを過剰の生理食塩水中に３０分間浸漬し、その後金網上に乗せ、１０Kgの荷重をかけて２０分間水切りし、増加重量を測定して吸収量とした。

・リウェット量：人工尿５０ｍｌをモデル紙おむつの中央部に注ぐ。１０分後、紙おむつの中央部に１０ｃｍ×１０ｃｍの沪紙１０枚を重ねて置き、沪紙の上から３．５ｋｇの荷重を均等に乗せる。３分後に沪紙の増加重量を測定し、この値をリウェット量とする。リウェット量が少ないほどモデル紙おむつのドライ感は良好である。

・人尿中で１０時間保持した後の吸収量：モデル紙おむつをアンモニア産生菌を添加した３７℃の新鮮人尿（５名の人尿を混ぜ合わせた尿）中に１０時間浸して吸収、保存した後、金網上に乗せ、１０Ｋｇの荷重をかけて２０分間水切りし、増加重量を測定して人尿中で１０時間保持した後の吸収量とした。

【００５５】実施例１

容量１リットルのガラス製反応容器にアクリル酸ナトリウム７６．６ｇ、アクリル酸２３ｇ、Ｎ，Ｎ'-メチレンビスアクリルアミド０．４ｇおよび脱イオン水２９５ｇを仕込み、撹拌・混合しながら内容物の温度を５℃に保った。内容物に窒素を流入して溶存酸素量を１ｐｐｍ以下とした後、過酸化水素の１％水溶液１ｇ、アスコルビン酸の０．２％水溶液１．２ｇおよび２，２'-アゾビスアミジノプロパンジハイドロクロライドの２％水溶液２．４ｇを添加して重合を開始させ、約５時間重合することにより吸水性樹脂濃度２５％の含水ゲル状重合体（１）を得た。この含水ゲル状重合体（１）４００部をニーダーで混練しながらジデシルジメチルアンモニウム炭酸塩の３０％メタノール／水混合溶液（メタノール／水比＝５０／５０質量％）３部を添加して均一に混練した。この混練物を９０℃で減圧乾燥し、ピンミルで粉砕した後、８５０～１５０ミクロンの粒度が約９５％となるように粒度調整して抗菌性吸水剤を得た。この抗菌性吸水剤の性能測定結果を表１および表２に示す。

【００５６】実施例２

実施例１において、ジデシルジメチルアンモニウム炭酸塩の３０％メタノール／水混合溶液に代えて、ジドデシルジメチルアンモニウム炭酸塩の３０％メタノール／水混合溶液を同量使用する以外は実施例１と同様にして抗菌性吸水剤を得た。この抗菌性吸水剤の性能測定結果を表１および表２に示す。

【００５７】実施例３

市販の吸水性樹脂（「サンウェットＩＭ－１０００」三洋化成工業製；デンプン－アクリル酸ナトリウム塩共重合体の架橋物；中和度７０モル％）１００部に水４００部を吸収させて含水ゲル状物を得た。この含水ゲル状物に実施例１と同じジデシルジメチルアンモニウム炭酸塩（３０％メタノール溶液）３部を添加してニーダーで均一に混練後、実施例１と同様にして乾燥、粉砕、粒度調整して抗菌性吸水剤を得た。この抗菌性吸水剤の性能測定結果を表１および表２に示す。

【００５８】実施例４

市販の吸水性樹脂（「サンウェットＩＭ－５８００」三洋化成工業製；架橋ポリアクリル酸の７２モル％中和ナトリウム塩を表面架橋した表面架橋型吸水性樹脂）１００部を家庭用ミキサーで高速撹拌しながら、ジデシルジメチルアンモニウム炭酸塩の２０％メタノール／水混合溶液（メタノール／水比＝５０／５０質量％）４．５部を少しづつ添加して均一に混合し、抗菌性吸水剤を得た。この時の混合温度は２４℃であった。この抗菌性吸水剤の性能測定結果を表１および表２に示す。

【００５９】実施例５

実施例４において、ジデシルジメチルアンモニウム炭酸塩の２０％メタノール／水混合溶液に代えて、オクチルトリメチルアンモニウム炭酸塩の２０％メタノール／水混合溶液を同量使用する以外は実施例４と同様にして抗菌性吸水剤を得た。この抗菌性吸水剤の性能測定結果を表１および表２に示す。

【００６０】実施例６および７

実施例４において、ジデシルジメチルアンモニウム炭酸塩（２０％メタノール／水混合溶液）の添加量を０．４５部（実施例６）、あるいは９部（実施例７）に代える以外は実施例４と同様にして抗菌性吸水剤およびを得た。これらの抗菌性吸水剤の性能測定結果を表１および表２に示す。

【００６１】試験例

実施例１及び実施例３～７で得られた抗菌性吸水剤を、各々の坪量が１００ｇ／m^2である２層のパルプ間に６０g/m^2の割合で均一に散布してサンドイッチし、５ｋｇ／ｃm^2の圧力でプレスした。この下層にポリエチレンフィルムを、上層にポリプロピレン不織布を重ね合わせた後、１４ｃｍ（幅）×３５ｃｍ（長さ）のサイズに切断することにより吸収性物品を作成した。実施例１の抗菌性吸水剤および実施例３～７の抗菌性吸水剤～を使用して得られた吸収性物品（ａ）、（ｂ）、（ｃ）、（ｄ）、（ｅ）および（ｆ）の性能測定結果を表３に示す。

【００６２】比較例１

実施例１で得た含水ゲル状重合体（１）を９０℃で減圧乾燥し、ピンミルで粉砕した後、８５０～１５０ミクロンの粒度が約９５％となるように粒度調整して比較の吸水性樹脂粉粒体＜１＞を得た。＜１＞の性能測定結果を表１および表２に示す。

【００６３】比較例２および３

「サンウェットＩＭ－１０００」および「サンウェットＩＭ－５８００」の性能測定結果を比較例２および比較例３として表１および表２に示す。

【００６４】比較例４

実施例４において、市販の吸水性樹脂（三洋化成工業製、「サンウェットＩＭ－５８００」）１００部を家庭用ミキサーで高速撹拌しながら、塩化ベンザルコニウムの１０％水溶液９部を噴霧添加して均一に混合し乾燥させて、比較の抗菌性吸水剤＜２＞を得た。可能な限り均一な分散状態を得ようとしたが、多少の塊状物の生成が認められた。＜２＞の性能測定結果を表１および表２に示す。

【００６５】比較例５

実施例４において、市販の吸水性樹脂（三洋化成工業製、「サンウェットＩＭ－５８００」）１００部を家庭用ミキサーで高速撹拌しながら、セチルトリメチルアンモニウムクロライドの２０％メタノール／水混合溶液（メタノール／水比＝５０／５０質量％）４．５部を添加して均一に混合し、比較の抗菌性吸水剤＜３＞を得た。＜３＞の性能測定結果を表１および表２に示す。

【００６６】比較試験例

試験例に記載の内容と同様にして、比較例１～５の吸水性樹脂粉粒体または抗菌性吸水剤を使用して吸収性物品（ｇ）、（ｈ）、（ｉ）、（ｊ）および（ｋ）を得た。これらの比較の吸収性物品の性能測定結果を表３に示す。

【００６７】

【表１】

【００６８】　　【表２】

		アンモニア産生菌での抗菌性（菌株数／ｍｌ）		人尿中１０時間後の吸収量（ｇ／ｇ）
		２時間後	１０時間後	
実施例	１	４．９×１０^{2}	２．８×１０^{2}	５４
	２	５．８×１０^{2}	６．５×１０^{2}	５６
	３	２．３×１０^{2}	８．４×１０	５８
	４	＜５	＜５	５７
	５	７．８×１０^{2}	９．５×１０^{2}	５６
	６	４．１×１０^{2}	１．８×１０^{3}	５３
	７	０	０	５７
－	－	－	－	－
比較例	１	６．３×１０^{8}	５．５×１０^{9}	２８
	２	７．７×１０^{8}	８．４×１０^{9}	２６
	３	７．５×１０^{8}	８．３×１０^{9}	３４
	４	５．８×１０^{4}	２．２×１０^{5}	２９
	５	１．６×１０^{3}	３．８×１０^{3}	４２

【００６９】　　【表３】

吸収性物品		吸収量（ｇ／枚）	リウェット量（ｇ）	悪臭防止テスト	人尿中１０時間後の吸収量（ｇ／ｇ）
試験例	ａ	４６０	０．３	１．６	４５０
	ｂ	４９０	０．２	１．２	４８５
	ｃ	４７０	０．３	１．４	４６０
	ｄ	４７５	０．２	１．８	４７０
	ｅ	４７５	０．２	２．０	４５０
	ｆ	４７０	０．１	０．８	４７０
比較試験例	ｇ	４８５	０．３	４．４	３９０
	ｈ	４８５	０．５	４．６	３７０
	ｉ	４７５	０．４	４．１	４００
	ｊ	４６５	０．８	３．２	３９５
	ｋ	４７０	０．５	２．４	４３５

【００７０】

【発明の効果】本発明の抗菌性吸水剤は次のような特徴および効果を有する。

優れた吸収機能と、優れた抗菌機能とを同時に発現する。特に、アンモニア産生菌に対する抗菌作用に優れることから、アンモニア臭の発生が防止できる。

吸水剤に吸収された尿、血液、体液などに含まれる有機物が菌類、微生物、バクテリアなどの作用によって腐敗するのを抑制することができる。また、腐敗が抑制される結果、悪臭の発生が少ない。

人尿中においても長時間にわたって安定した吸収性能を発現する。

従来の吸水性樹脂と吸着成分や消臭成分を単に混合したものでは、振動や衝撃によって両者の分離を生じたり、吸収性物品に適用した際に吸収性物品内で吸水性樹脂と吸着成分あるいは消臭成分とが遍在を起こす心配があったが、本発明の吸水剤は抗菌剤成分が吸水性樹脂に固定されているため、粉体特性（粉体流動性、発塵性など）の悪化がなく、分離や偏在の心配が無い。

紙おむつ、生理用品などの吸収性物品に適用することにより、吸収性物品に抗菌機能を付与することができて悪臭の発生を抑制し、皮膚刺激やかぶれの発生が少なくなると共に、吸収性物品の吸収性能も長時間にわたって良好である。

【００７１】上記効果を奏することから、本発明の抗菌性吸水剤は、大人および子供用の紙おむつ、失禁者用パッド、生理用ナプキン、パンティーライナー、母乳パッド、産褥用マット、医療用アンダーパッドなど、各種吸収性物品に特に有用である。さらに、ペット尿や廃血液など、腐敗により悪臭を発生する各種体液のゲル化剤や排泄物処理剤に有用である。また、ペット尿吸収シート、ドリップ吸収材などのシート状あるいはテープ状の吸収性物品を製造する際にも有用である。その他、吸水性樹脂に水を吸水させたゲルを利用する用途（例えば、保冷材、人工雪、ウオーターベッドなど）やヘドロ固化剤、結露防止壁材など、腐敗により悪臭の発生を伴う用途にも有用である。

フロントページの続き

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CLAIMS

[Claim(s)]
[Claim 1]An antibacterial water absorption agent in which has an acid radical in a side chain and at least some acid radicals exist in a form of quarternary ammonium salt and which content of the 4th class nitrogen atom becomes from hydrophilic resin (A) which is $2x10^{-4}$ - 0.8 mass %.
[Claim 2]The antibacterial water absorption agent according to claim 1 whose acid radical which exists in a form of quarternary ammonium salt in hydrophilic resin (A) is a basis shown with a following general formula (1).

$$-X^- \cdot [R_1-\underset{\displaystyle R_4}{\overset{\displaystyle R_2}{\overset{|}{\underset{|}{N}}}}-R_3]^+ \qquad (1)$$

X^- is the anion group which carried out the covalent bond to a polymer chain in hydrophilic resin (A) among [type, R_1 - R_4 are organic groups, and two bases chosen from R_1-R_4 may join mutually together, and they may form a ring. At least one of R_1 - R_4 is an aliphatic hydrocarbon group of the carbon numbers 5-20.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Art in which an invention belongs] This invention is excellent in absorption performance, antibacterial performance, and particulate flow kinesis, and relates to the absorbent article using an antibacterial water absorption agent and this useful to the absorbent article which absorbs urine, blood, body fluid, etc. especially.
[0002]
[Description of the Prior Art]Hydrophilic resin is used using the absorption performance, water retention ability, and gelling capacity by various applications, such as absorbent articles, such as a pad for a disposable diaper, an incontinence pad, a sanitary napkin, and mother's milk, the sheet for pets, the floor sand for pets, an excrement processing agent, a

waste blood gelling agent, a drip absorbent, a freshner. However, although conventional hydrophilic resin is excellent in the capability to absorb and retain urine, blood, body fluid, etc., it does not have the antibacterial function.
[0003]Therefore, when conventional hydrophilic resin absorbs fluids, such as urine, blood, and body fluid, the organic matter contained in a lean solution is disassembled by fungi, microorganism, etc., and there is a problem that this decomposition product becomes causes, such as offensive odor generating, a skin stimulus, a rash. It is easy to decompose water absorption gel by the bacteria in the air, etc., and an offensive odor may be emitted by putrefaction.
[0004]From the above thing, an appearance of a material excellent in the both sides of a water absorption function and an antibacterial function has been desired from a viewpoint of a sanitary aspect and safety. Especially in absorbent articles used for a bedridden elderly, a sick person, etc., such as an adult paper diaper and a pad for incontinentia persons, the problem of an offensive odor or a rash is serious and solution is desired. When discarding a further used absorbent article, an appearance of the hydrophilic resin which has the antibacterial function outstanding also from the purpose of preventing infection by a disease germ etc. is desired.
[0005]as the method of making the effect near the above revealing -- the mixture (JP,57-25813,A.) of the granular materials of ** hydrophilic resin and zeolite JP,59-179114,A, JP,59-189854,A, ** The constituent which coated activated carbon with hydrophilic resin (JP,56-31425,A), ** The constituent which comprises hydrophilic resin and the deodorizing component extracted from the Theaceae vegetation (JP,60-158861,A), ** The hydrophilic resin constituent containing a specific germicide (a benzalkonium chloride, chlorhexidine glyconate) (JP,4-17058,B), ** Application to the hydrophilic resin constituents (JP,5-179053,A) containing a phosphate compound and these absorbent articles is proposed.
[0006]
[Problem(s) to be Solved by the Invention]However, the constituent of these ** - ** had the problem that neither the offensive odor occurrence prevention effect not necessarily satisfying to applying to an absorbent article nor putrefaction depressor effect was acquired, or absorption performance fell by putrefaction etc. In order to satisfy an antibacterial function or a deodorizing function, post-processing of the substance which has these functions needed to be carried out to hydrophilic resin, but there was a problem that the particulate flow kinesis of the constituent obtained by this post-processing fell.
[0007]Namely, mixture ** of hydrophilic resin and zeolite, Since the hydrophilic resin and zeolite of what can adsorb to some extent and can demonstrate a deodorant effect do not have an antibacterial function, the generated offensive odor cannot control decomposition or putrefaction of a microorganism or the organic matter by fungi, and cannot prevent generating of an offensive odor. Therefore, even if applied to the absorbent article, a skin stimulus, a rash, etc. by disassembly of an organic matter were not able to be stopped. The degree of raising dust became high because zeolite separates from hydrophilic resin by vibration or a shock, and variation was looked at by the deodorizing function.
[0008]In the case of constituent ** which coated activated carbon with hydrophilic resin, and constituent ** which comprises hydrophilic resin and the deodorizing component extracted from the Theaceae vegetation. A case of the above-mentioned zeolite and same

result were brought from the deodorizing component extracted from activated carbon and the Theaceae vegetation not showing an antibacterial function, and putrefaction of a microorganism or the organic matter by fungi was not able to be controlled. Since these were fixed in hydrophilic resin when using adsorbent like the zeolite of **, and the deodorizer extracted from the Theaceae vegetation of **, there was a problem of needing special operation.

[0009]Hydrophilic resin constituent ** containing a benzalkonium chloride or chlorhexidine glyconate or hydrophilic resin constituent ** containing a phosphate compound, Although a certain amount of germicidal action is accepted, the fungi which are the targets of a sterilization use, and the kind of microorganism have limitation, and satisfaction is necessarily impossible. Although the antibacterial effect over Escherichia coli or the Candida bacillus is excellent, especially a benzalkonium chloride, From a comparatively low thing, the antibacterial action to an ammonia production bacillus (Providentica rettgeri). Generating of ammonia by the organic matter in urine decomposing cannot be controlled thoroughly, but urinary pH changes with the ammonia which remains to alkalinity, and there is a problem that water absorption capacity falls as a result. The antibacterial hydrophilic resin constituent produced by processing with these antimicrobial agents had the problem that particulate flow kinesis fell depending on the throughput of an antimicrobial agent.

[0010]

[Means for Solving the Problem]This invention persons are excellent in absorption performance and particulate flow kinesis in view of the above-mentioned problem, An antibacterial action outstanding to especially an ammonia production bacillus was revealed, there was no fall of absorption performance also in the state where urine was absorbed, and this invention was reached as a result of examining a useful antibacterial water absorption agent wholeheartedly to an absorbent article used in order to absorb urine, blood, body fluid, etc.

[0011]That is, this inventions are an antibacterial water absorption agent of following [1] and [2], and an antibacterial absorbent article of [3].

[1] An antibacterial water absorption agent in which has an acid radical in a side chain and at least some acid radicals exist in a form of quarternary ammonium salt and which content of the 4th class nitrogen atom becomes from hydrophilic resin (A) which is $2x10^{-4}$ - 0.8 mass %.

[2] An absorbed amount to ** physiological saline (0.9% sodium chloride aqueous solution) is a water absorption agent which consists of at least one sort of hydrophilic resin of 30 or more g/g, ** At least one sort of hydrophilic resin has an acid radical in a side chain, and does $2x10^{-4}$-0.8 mass % content of the 4th class nitrogen atom into ** water absorption agent ingredient, ** An antibacterial water absorption agent, wherein an absorbed amount after a viable cell equity volume measured by a mixture plate culture method after inoculating an ammonia production bacillus into a water absorption agent and cultivating for 2 hours having 1/10,000 or less antibacterial action of an early viable cell equity volume and holding in ** human urine for 10 hours is 30 or more g/g.

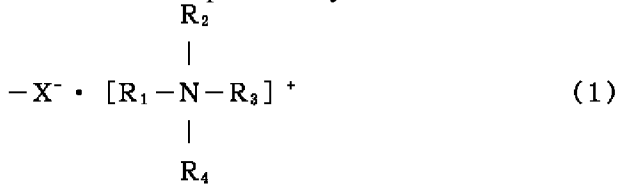
[3] An antibacterial absorbent article in which an antibacterial water absorption agent the above [1] or given in [2] paragraphs has the layer held in fibrous support of absorptivity.

[0012]

[Embodiment of the Invention]In the antibacterial water absorption agent [1] of this

invention, hydrophilic resin (A) has an acid radical in a side chain, and at least some acid radicals exist in the form of quarternary ammonium salt. Therefore, hydrophilic resin (A) is the resin which the water absorption capacity which hydrophilic resin has, and the antibacterial performance by operation of the acid radical which exists in the form of quarternary ammonium salt had.

[0013]As a suitable example, the basis shown at the following general formula (1) is mentioned in the viewpoint of the antibacterial performance of the acid radical which exists in the form of quarternary ammonium salt in this hydrophilic resin (A).



$$-X^- \cdot [R_1-\underset{\displaystyle R_4}{\overset{\displaystyle R_2}{\overset{|}{\underset{|}{N}}}}-R_3]^+ \qquad (1)$$

X^- is the anion group which carried out the covalent bond to the polymer chain in hydrophilic resin (A) among [type, R_1 - R_4 are organic groups, and two bases chosen from R_1-R_4 may join mutually together, and they may form the ring. At least one of R_1 - R_4 is an aliphatic hydrocarbon group of the carbon numbers 5-20.]

[0014]That is, at least one of the acid radicals which carried out the covalent bond to the polymer chain in this hydrophilic resin (A) is the structure which became group X for anion $^-$ of the 4th class ammonium cation, and formed the salt. As X^-, what is necessary is just the anion group which carried out the covalent bond to the polymer chain, Although there is no restriction in particular, carboxyl anion group-COO^-, sulfonate anion group-SO_3^-, a sulphate anion group, a phosphoric acid anion group, etc. are mentioned, and desirable things are a carboxyl anion group and a sulfonate anion group, especially a carboxyl anion group. R_1, R_2, R_3, and R_4 are the viewpoints of antibacterial performance, and it is [at least one] preferably preferred a hydrocarbon group and that it is an aliphatic hydrocarbon group, especially an alkyl group more preferably, and is an alkyl group of the carbon numbers 5-20.

[0015]Hydrophilic resin (A) is a range from which the content of the 4th class nitrogen atom usually becomes $2x10^{-4}$ - 0.8 mass %, and at least some acid radicals exist in the form of quarternary ammonium salt. converting the content of the acid radical of the form of quarternary ammonium salt in this hydrophilic resin (A) into the content of the 4th class nitrogen atom to the mass of this resin -- usually -- $2x10^{-4}$ - 0.8 mass % -- desirable -- $1x10^{-3}$ - 0.4 mass % -- they are $2x10^{-3}$ - 0.1 mass % especially.

[0016]The remaining acid radical that is not a form of quarternary ammonium salt is usually an acid radical neutralized by unneutralized an acid radical and/or alkali metal salt, ammonium salt, or amine salt. As an acid radical in this hydrophilic resin (A), a carboxyl group, a sulfonic group, One or more sorts chosen from a sulfuric acid group, phosphate groups, and these salts are mentioned, and what was neutralized as what has not continued neutralizing these as mentioned above, alkali metal salt, etc., and the thing which exists in the form of quarternary ammonium salt are intermingled as a side chain.

[0017]As for this hydrophilic resin (A), what has the carboxyl group neutralized by the thing which has the carboxyl group neutralized by a carboxyl group and/or alkali metal salt, ammonium salt, or amine salt as a side chain especially a carboxyl group, and/or alkali metal salt as a side chain is preferred. The accompanying effect that the carboxyl

group which is not neutralized [the neutralization which remains except for the acid radical which exists in the form of quarternary ammonium salt thru/or] adsorbs ammonia etc. which are kinds of an odor component is acquired.
[0018]The shape of (A) is a grain, granularity, the shape of a granulation, the shape of a piece of Lynn, and massive especially preferably, although the shape of powder may be preferred, for example, may be which shape, such as a grain, granularity, the shape of a granulation, the shape of a piece of Lynn, mass, the shape of a pearl, and the shape of impalpable powder, from a viewpoint of water absorption capacity. Although there is no limitation in particular also about a particle size or particle size distribution, 90 % of the weight or more is 1 mm or less preferably, and 90 % of the weight or more is [95 % of the weight or more] 0.1-0.9 mm 0.1-0.9 mm still more preferably especially.
[0019]30 or more g/g of absorption power to the physiological saline (0.9% of sodium chloride aqueous solution) of (A) are 40 - 75 g/g 35 to 80 g/g still more preferably especially preferably. Absorption power is measured by the method of mentioning later.
[0020]Hydrophilic resin (A) is obtained by the operation which makes at least some acid radicals of the hydrophilic resin (a) which has an acid radical in a side chain the form of quarternary ammonium salt, for example. Illustration of the suitable process of hydrophilic resin (A) will obtain hydrophilic resin (A) by making the hydrophilic resin (a) which has an acid radical, and the 4th class ammonium carbonate (b) react to a side chain under existence of water.
[0021]. The carbonate anion which constitutes (b), and at least one of the acid radicals in (a) carry out anion exchange of this reaction. That is, the anion of (a) runs by the reaction used as the opposite anion of the 4th class ammonium cation of (b), and in order for a carbonate anion to serve as carbon dioxide by a reaction and to evaporate it, there is no survival of a by-product, and there is an advantage from which quarternary-ammonium-salt group content hydrophilic resin with high purity is obtained. Not the meaning of making the above-mentioned reaction not necessarily react 100% but unreacted (b) may remain in (A) to some extent. That is, the state where the salt was formed as the 4th class ammonium cation, and the state of the 4th class ammonium carbonate may live together. The cross linking agent which has two or more functional groups which can react to the acid radical of (a) can be made to be able to live together, and the structure of cross linkage can also be introduced simultaneously with (a) and a reaction with (b).
[0022]As the above-mentioned hydrophilic resin (a) which can be used for manufacture of hydrophilic resin (A), what has the acid radical neutralized by unneutralized an acid radical and/or alkali metal salt, ammonium salt, or amine salt is suitably used for a side chain -- the degree of neutralization of the acid radical in hydrophilic resin (a) -- desirable -- 50-80 Eq -- % -- 60-75 Eq is % especially. The value of equivalent % says here % of the basis by which it was neutralized of the acid radicals. As hydrophilic resin (a) which has an acid radical in a side chain, If the acid radical which is not neutralized [of a carboxyl group, a sulfonic acid group, a sulfuric acid group, a phosphate group, etc.] to the constitutional unit and/or these are hydrophilic resin which has the basis neutralized as alkali metal salt, ammonium salt, or amine salt in a side chain, a kind and a manufacturing method in particular will not be limited. Usually, the acid radical in (a) which is not neutralized keeps for a reaction with the 4th class ammonium carbonate (b).
[0023]The hydrophilic resin which has a carboxyl group and/or its salt as a suitable example of hydrophilic resin (a) (a1), The hydrophilic resin (a3) etc. which have

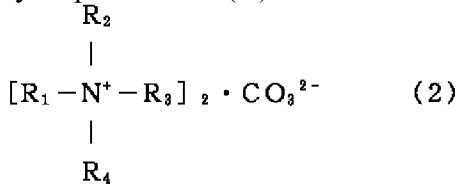
hydrophilic resin (a2) which has a sulfonic group and/or its salt, a phosphate group, and/or its salt are mentioned, and these examples are as follows. As an example of the hydrophilic resin (a1) which has a carboxyl group and/or its salt, - The bridge construction thing of a starch acrylic acid (salt) copolymer given in JP,53-46199,B and JP,53-46200,B each gazette, - The polyacrylate by an opposite phase suspension polymerization method given in JP,54-30710,B and JP,56-26909,A each gazette by which bridge construction or self-bridge construction was carried out, - Aqueous polymerization given in JP,55-133413,A etc. (it and) [heat-insulation-] The bridge construction polyacrylic acid obtained by an application-of-pressure polymerization, a thin film polymerization, spray polymerization, etc. (salt), - Vinyl ester given in JP,52-14689,A and JP,52-27455,A each gazette, unsaturated carboxylic acid, or a copolymer saponification thing with the derivative, - An isobutylene-maleic anhydride copolymer bridge construction thing, the hydrolyzate of a starch acrylonitrile copolymer, A bridge construction carboxymethyl cellulose derivative, the copolymer bridge construction thing of acrylic acid (salt) and acrylamide, an acrylamide polymer bridge construction thing, or its partial hydrolysate is mentioned. Two or more sorts of above-mentioned hydrophilic resin (a1) may be used together. The surface crosslinking type hydrophilic resin to which surface crosslinking of the neighborhood of the surface of the powder of the above-mentioned hydrophilic resin (a1) is carried out further can also be used conveniently for this invention. The methods (the kind of surface crosslinking agent, an addition, the conditions made to construct a bridge, etc.) of surface crosslinking can apply a publicly known method.

[0024]The bridge construction polyacrylic acid (salt) etc. which carried out copolymerization of the sulfonic group content monomer of a statement to JP,58-2312,A and JP,61-36309,A each gazette as an example of hydrophilic resin (a2) of having a sulfonic acid group and/or its salt are mentioned. As an example of the monomer which has a sulfonic acid group used for the hydrophilic resin which replaced a part of carboxyl group in such hydrophilic resin by the sulfonic acid group, Aliphatic series or aromatic vinyl SUFON acid [vinylbenzene sulfonic acid,], such as allylsulfonic acid, vinyltoluene sulfonic acid, and styrene sulfonic acid, (Meta) Acrylic sulfonic acid [(meta) acrylic acid sulfoethyl, acrylic acid (meta) sulfopropyl], etc., acrylamide (meta) sulfonic acid [2-acrylamido-2-methyl propane sulfonic acid], etc. are mentioned.

[0025]The hydrophilic resin which replaced a part of carboxyl group in the above-mentioned bridge construction polyacrylic acid (salt) by the monomer which has a phosphate group as an example of hydrophilic resin (a3) of having a phosphate group and/or its salt is mentioned. As an example of a monomer of having a phosphate group, meta-KURIROIDOKISHI ethyl phosphate, acryloid KISHIE chill phosphate, etc. are mentioned.

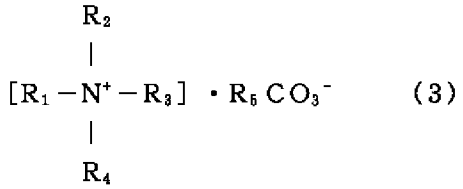
[0026](a1) A desirable thing is a carboxyl group and/or its salt hydrophilic resin (a1) which it has among - (a3), and a still more desirable thing, It is hydrophilic resin of the insoluble in water nature which makes acrylic acid and acrylate a main constitution unit in that reactivity is excellent when demonstrating comparatively big absorptance and making quarternary ammonium salt form. Although the salts which neutralized the acid radical in this hydrophilic resin (a) are usually alkali metal salt, such as sodium salt and potassium salt, they may be the organic salt of ammonium salt, amine salt, etc. depending on a use.

[0027]In the hydrophilic resin (a1) which has a carboxyl group and/or its salt, the degree of neutralization of a carboxyl group is 60 to 75% 50 to 80% especially preferably as aforementioned. If hydrophilic resin (a1) is used, when the hydrophilic resin (A) derived has a carboxyl group, The accompanying effect that the carboxyl group in which a carboxyl group remains except for the portion which exists in the form of quarternary ammonium salt adsorbs ammonia etc. which are kinds of an odor component is acquired as above-mentioned. When the degree of neutralization of a carboxyl group is less than 50%, absorption performance falls, and pH of the antibacterial water absorption agent obtained serves as acidity, and is not preferred in respect of the safety to the skin. When the degree of carboxyl group neutralization exceeds 80%, while the effect of adsorbing ammonia etc. becomes scarce, pH of the antibacterial water absorption agent obtained serves as alkalinity, and is not preferred in respect of safety [as opposed to the skin in this case].
[0028]The compound shown with the following general formula (2) or (3) as an example of the above-mentioned 4th class ammonium carbonate (b) which can be used for manufacture of hydrophilic resin (A) is mentioned.



(2)

[0029]



(3)

Among [each formula, an organic group and R_5 are low-grade alkyl groups, two bases chosen from R_1-R_4 may join mutually together, and R_1 - R_4 may form the ring.]
[0030]When (b) is a compound of a general formula (2), a reaction with (a) generates lower alcohol with carbon dioxide, but whether it dissolves in water, and in order to evaporate, there is no survival of a by-product too and resin with high purity (A) is obtained. The compound shown by the general formula (2) or (3) is compoundable by the reaction of the tertiary amine (b1) and diester carbonate (b2) which have at least one aliphatic series alkyl group of the carbon numbers 5-20.
[0031]As (b1), octyldimethylamine, decyldimethylamine, Lauryl dimethylamine, milli cetyldimethyl amine, cetyldimethyl amine, Stearyldimethylamine, dihexylmethylamine, dioctylmethylamine, didecylmethylamine, didodecylmethylamine, 2-heptadecenyl hydroxyethyl imidazoline, etc. are mentioned. A desirable thing is tertiary amine which has two aliphatic series alkyl groups of the carbon numbers 5-20, and still more desirable things are dioctylmethylamine and didecylmethylamine. Although dimethyl carbonate, diethyl carbonate, ethyl carbonate methyl, and dipropyl carbonate are mentioned as (b2), since dimethyl carbonate with few carbon numbers of an alkyl group is excellent in reactivity, it is desirable.

[0032]the mole ratio of the tertiary amine (b1) and diester carbonate (b2) at the time of manufacture of the 4th class ammonium carbonate (b) -- usually -- 1: (0.3-4.0) -- it is 1: (0.5-2.5) preferably, and 30-150 ** of reaction temperature is usually 50-120 ** preferably. A solvent like methanol or ethanol or the mixed solvent of these and water can be used as occasion demands.
[0033]The content of the 4th class nitrogen atom in (A) should just make the hydrophilic resin (a) at the time of manufacturing this hydrophilic resin (A), and the ratio with the 4th class ammonium carbonate (b) a ratio which becomes said within the limits, and can change them variously by balance of the absorption performance and antibacterial performance which are made into the purpose. usually, the ratio of (a): (b) -- the acid radical in (a), and the equivalent ratio of (b) -- 1: ($3x10^{-5}$ - 0.3) -- desirable -- 1: ($1x10^{-4}$ - 0.1) -- it is 1: ($3x10^{-4}$ - $8x10^{-2}$) still more preferably. The antibacterial effect of the constituent in which the equivalent ratio of (b) is obtained by less than $3x10^{-5}$ becomes scarce. On the other hand, in order that the equivalent ratio of (b) may demonstrate antibacterial effect sufficient by 0.3, even if it raises a ratio more, the antibacterial effect is unnecessary from hardly increasing.
[0034]Furthermore it makes the 4th class ammonium carbonate compound (b) react to the hydrophilic resin (a) which has an acid radical under existence of water and obtains this hydrophilic resin (A), as a concrete method, for example, the method of following the (1) - (4) is mentioned, and the method of of (1) and (4) is preferred.
(1) How to make it react and to make quarternary ammonium salt form near the surface of the powder of hydrophilic resin after mixing the aquosity liquid of the 4th class ammonium carbonate (b) to the powder of hydrophilic resin (a).
How to heat, react and dry and grind after kneading (b) to the hydrous gel-like polymer obtained by the manufacturing process of (2) and (a).
the method of coming out of, kneading and heating (b), making react and dry it, and grinding, after making (3) and (a) absorb water and creating water absorption gel.
(4) and (a) are made to absorb the solution of (b), and after creating and kneading hydrous gel, the method of heating, reacting and drying and grinding is mentioned.
[0035](1) The quantity of the water used in the method of - (4) is usually 5 - 450 mass part preferably one to 500 mass part to (a)100 mass part. if trouble does not have the quantity of water in the reaction of (a) and (b) at less than one mass part when the reaction of (a) and (b) does not fully advance but exceeds 500 mass parts on the other hand, but a lot of water is evaporated after that and it is **** -- ** -- it is not economical.
[0036]The above (1) In the method of - (4), there is no limitation in particular about the industrial device which mixes (b) with (a), and a publicly known device can be used from the former. For example, as an industrial device which mixes the powder of (a), and the solution of (b), An omnipotent mixer, a turbulizer, a NAUTA type mixer, a ribbon blender, a conical blender, a V shaped rotary mixer, a screw-type mixer, a fluid bed type mixer, a spray mixer, mortar MOKISA, etc. are mentioned. As an industrial device which kneads (b), a kneader, one axis or a biaxial extrusion mixer, an omnipotent mixer, a gear compounder, a minced meat machine, a NAUTA type mixer, a screw type mixer, etc. are mentioned to the hydrous gel or water absorption gel of (a), for example.
[0037]Although there is no limitation in particular about the temperature which makes (b) react to (a), the method of the following ** and ** can be illustrated.
** Like the method of the above (1), (a) of 1-150 ** at the time of making it react is 10-

130 ** especially preferably, when powdered.
** The above (2) Like the method of - (4), (a) at the time of making it react is hydrous gel-like, and in a reaction, when desiccation is required, it is 40-130 ** 40-150 ** especially preferably. A reaction and desiccation can also be made to perform under decompression as occasion demands. If the coagulation of water takes place below 0 ** and temperature exceeds 150 ** on the other hand undesirably, decomposition may be produced depending on the kind of (b) and it is not desirable.
[0038]As for both, being mixed uniformly is [the water absorption agent [1] of this invention] preferred so that the usual hydrophilic resin (A') which does not have the 4th class ammonium may be contained and uniform antibacterial performance may be demonstrated in this case with this hydrophilic resin (A). It is necessary to make content of the 4th class nitrogen atom which (A) in the total mass of hydrophilic resin (A) and (A') has more than $2x10^{-4}$ mass % from a viewpoint of antibacterial performance in this case, and this quantity of more than $1x10^{-3}$ mass % is more than $2x10^{-3}$ mass % especially preferably.
[0039]The range with preferred absorption power to the physiological saline of hydrophilic resin (A') is the same as that of hydrophilic resin (A), and there is no limitation in particular also about the kind of resin. The example of representation of this hydrophilic resin (A') is hydrophilic resin (a) which has an acid radical in the side chain illustrated above, and that also of the desirable thing and the degree of neutralization in (a) is the same as that of the above. The range of the shape and the particle size of hydrophilic resin (A'), and particle size distribution is the same as that of hydrophilic resin (A).
[0040]An absorbed amount [as opposed to a physiological saline (0.9% sodium chloride aqueous solution) in the water absorption agent [2] of this invention] consists of at least one sort of hydrophilic resin of 30 or more g/g, and at least one sort of this hydrophilic resin has an acid radical in a side chain. $2x10^{-4}$-0.8 mass % content of the 4th class nitrogen atom is done into the ingredient of a water absorption agent [2].
[0041]The water absorption agent [2] of this invention is excellent not only in the antibacterial action to Escherichia coli but the antibacterial action to an ammonia production bacillus as compared with the publicly known antibacterial hydrophilic resin constituent (for example, constituent given in JP,4-17058,B) which uses a benzalkonium chloride. That is, the viable cell equity volume measured by the mixture plate culture method after inoculating the ammonia production bacillus and cultivating for 2 hours is reduced by 1/10,000 or less [of an early viable cell equity volume], and has the outstanding operation that generating of ammonia can be prevented. Evaluation of an antibacterial effect and the amount of ammonia productions is measured by the method of mentioning later.
[0042]The absorbed amount after holding in [of the water absorption agent [2] of this invention] human urine for 10 hours is 30 or more g/g usually 40 - 75 g/g 35 to 80 g/g especially preferably. The absorbed amount after holding in human urine for 10 hours is measured by the method of mentioning later.
[0043]the above -- the following are illustrated as an example of an embodiment of the water absorption agent [2] of this invention which has the feature in composition [like], water absorption capacity, and antibacterial performance.
(1) The water absorption agent which the absorbed amount to said hydrophilic resin (A)

[physiological saline becomes from selection] about the thing of 30 or more g/g.
The mixture ratio from which the uniform mixture [4th class nitrogen atom of (2), (A), and said hydrophilic resin (A') becomes $2x10^{-4}$ - 0.8 mass %. (A) -- and an absorbed amount [as opposed to a physiological saline in (A')] -- the thing of 30 or more g/g -- selection]
(3) -- the absorbed amount to (A) [physiological saline -- a not less than 30g/g thing -- selection] and said the 4th class ammonium carbonate -- a uniform mixture with (b [what has an organic group of said R_1, R_2, R_3, and R_4]).
The mixture ratio from which the uniform mixture [4th class nitrogen atom of (4), (A), (A'), and (b) becomes $2x10^{-4}$ - 0.8 mass %. (A), (A'), and (b) -- the same thing] as (2) and (3) paragraphs
[0044]The water absorption agent [1] of this invention and [2] are the ranges which do not spoil operation effects, such as the water absorption capacity and antibacterial performance, necessity -- hydrophilic resin -- arbitrary processes -- as an extender and an additive agent -- an organic granular material (for example, pulp powder.) mineral matter (a silica dioxide and an aluminum oxide.), such as a cellulosic and a natural polysaccharide Magnesium oxide, aluminum silicate, a sodium silicate, a magnesium silicate, etc. should blend an antioxidant, a reducing agent, a chelating agent, a surface-active agent, a deodorizer, colorant, perfume, etc. Such quantity of below 10 mass % is usually below 5 mass % preferably to the mass of hydrophilic resin.
[0045]By applying the water absorption agent [1] of this invention, and/or [2] to various kinds of absorbent articles, the absorbent article excellent in the both sides of the water absorption effect and an antibacterial effect is obtained. As a method of applying a water absorption agent [1] and/or [2] to an absorbent article, A water absorption agent [1] and/or [2] should just form the layer held in the base material of absorptivity, For example, the method of mixing with fibrous material which carries out granule application, such as a method, pulp, and/or thermal melting arrival nature textiles, the method of sandwiching with the water absorption paper and the nonwoven fabric of two or more sheets, etc. are mentioned between the layers of fibrous material, such as pulp arranged in layers, thermal melting arrival nature textiles, or these mixtures.
[0046]The water absorption agent [1] of this invention and/or [2] have good particulate flow kinesis, and since they have the same handling fitness as conventional hydrophilic resin, they can manufacture an absorbent article with publicly known equipment from the former. The addition of the antibacterial water absorption agent to an absorbent article can be variously changed according to the kind of absorbent article, size, and target absorption performance. For example, in the case of a disposable diaper, an incontinence pad, the under pad for an operation, the mat for puerperia, etc., an absorbent article is usually 3-20g/sheet in addition, and, in the case of a sanitary napkin, a panty liner, a breast milk pad, the dressing material for wound side protection, etc., an absorbent article is usually 0.2-3g/piece. When applying to the sheet like object sandwiched with the water absorption paper and the nonwoven fabric of two or more sheets, a 10 - 80 g/m^2 grade is usually suitable.
[0047]
[Example]Hereafter, although an example and a comparative example explain this invention further, this invention is not limited to these. The effect check test of the absorbent article which uses the absorbed amount, the antibacterial effect, and the

antibacterial water absorption agent of the antibacterial water absorption agent itself was measured by the following method. Unless the following in particular sets, % shows mass %.

[0048](1) Absorbed amount : put 1.0 g of samples into the tea bag made from a nylon net of 250 meshes, by pulling up and hanging vertically, perform a drainer for 15 minutes and measure increased weight, after dipping this into a superfluous physiological saline (0.90% salt solution) for 1 hour and making it absorb. This increased weight was made into the absorbed amount.

[0049](2) Particulate flow kinesis : evaluation of particulate flow kinesis measured the angle of repose. Measurement of an angle of repose uses a powder tester (made by Hosokawa Micron CORP.), and it is made to flow out of the tip of the glass funnels of the attachment set under the sieve on an attached disk, after it puts an adequate amount for a sample calmly in a sieve (710 micrometers of openings), carrying out vibration and tapping. When the ridgeline of the deposited granular material became a fixed angle, the protractor was moved and the angle of repose was searched for so that the outflow of a sample might be stopped and the straight part of a protractor might become parallel in the ridgeline of the deposited granular material. It means that it is inferior to particulate flow kinesis, so that an angle of repose is large.

[0050](3) The antibacterial test of an antibacterial water absorption agent : carry out autoclave sterilization after putting 3.45 g of susceptibility bouillon culture media, and 150 ml of water into a 300-cc flask and dissolving in it. After making it swell, adding and stirring 1.0 g of test samples to this culture medium, Escherichia coli (bacillus number: JCM1649) was inoculated so that the early number of strains might serve as a $1x10^6$ individual / ml. Shaking culture of this sample is carried out at 37 **, it samples in 2 hours and 10 hours, and a sterilization isotonic sodium chloride solution performs stage dilution if needed. After putting this sampling article or 1 ml of dilution articles at a time into a sterilization petri dish, 20 ml of agar media are poured out, distributed solidification is uniformly carried out on a petri dish, and it cultivates for two days at 37 **. It is considered as a viable cell equity volume, carrying out a colony count after culture and applying dilution magnification. Viable cell equity volume measurement is performed by a mixture plate culture method. The viable cell equity volumes at the time of not adding a sample as blank on the other hand, but inoculating only Escherichia coli were a $6x10^9$ individual / ml after a $5x10^8$ individual / ml, and 10 hours after 2 hours. Antibacterial properties were similarly tested about the ammonia production bacillus. In this case, the ammonia production bacillus (Providentica rettgeri; bacillus number: IFO13501) was inoculated so that the early number of strains might serve as a $1x10^7$ individual / ml. The viable cell equity volumes at the time of not adding a sample as blank on the other hand, but inoculating only an ammonia production bacillus were a $4x10^9$ individual / ml after an $8x10^7$ individual / ml, and 10 hours after 2 hours.

[0051](4) The absorbed amount after holding in human urine for 10 hours : add 150 ml of fresh human urine (urine with which five persons' human urine was mixed), and the above-mentioned ammonia production bacillus to a 300-ml beaker, mix to it, and adjust solution temperature to 37 **. 1.0 g of samples are put into the tea bag made from a nylon net of 250 meshes, after dipping this into the above-mentioned liquid for 10 hours and absorbing and saving it, by pulling up and hanging vertically, a drainer is performed for 15 minutes and increased weight is measured. It was considered as the absorbed

amount after holding this increased weight in human urine for 10 hours.
[0052](5) effect check test [of the absorbent article which applied the antibacterial water absorption agent]: -- creation [of - absorbent article]: -- put the fluff pulp layer of the tissue paper of the same size, and basis weight 100 g/m^2 on the polyethylene sheet cut out in rectangle of 14 cm x 35 cm. Subsequently, 2.94 g of samples are uniformly sprinkled on fluff pulp, and also the fluff pulp layer, the tissue paper, and the nonwoven fabric of basis weight 100 g/m^2 are piled up in this order. A model disposable diaper is created by pressing this laminated material for 90 seconds by the pressure of 5 kg/cm^2.
- Offensive odor preventive effect test : make the center section of the model disposable diaper which applied the antibacterial water absorption agent add and absorb 80 ml of fresh urine, put into a 5-l. wide mouthed bottle, and seal. This is kept for 10 hours within the thermostat set as 40 **. Then, the lid of a wide mouthed bottle is opened within an odor free room, a smell is smelled, and odour strength is evaluated in the following six steps. Evaluation is carried out by the panelist of ten bad smell decision-capabilities confirmed Mino by T&T olfactometry, and calculates average value.
[0053]
0: No odor 1 : the smell which can be perceived at last (perception IKI value concentration)
2: it understands what smell it is -- weak -- stinking (cognitive IKI value concentration)
3: smell 4: which can be perceived comfortably -- strong smell 5: -- an intense smell
[0054](6) Performance test: and the absorbed amount which is an absorbent article : the model disposable diaper was immersed for 30 minutes into the superfluous physiological saline, and it put on the wire gauze after that, and it drained off water for 20 minutes, having applied 10 kg of load, increased weight was measured, and it was considered as the absorbed amount.
- The amount of RIWETTO : fill the center section of the model disposable diaper with 50 ml of artificial urine. Ten sheets of filter papers (10 cm x 10 cm) are put on the center section of the disposable diaper in piles in 10 minutes, and 3.5 kg of load is uniformly put from on a filter paper. The increased weight of a filter paper is measured in 3 minutes, and let this value be the amount of RIWETTO. The dry feeling of a model disposable diaper is so good that there are few amounts of RIWETTO.
The absorbed amount after holding in human urine for 10 hours : Dip a model disposable diaper for 10 hours into the 37 ** fresh human urine (urine with which five persons' human urine was mixed) which added the ammonia production bacillus, and - Absorption, It put on the wire gauze, after saving, it drained off water for 20 minutes, having applied 10 kg of load, and it was considered as the absorbed amount after measuring increased weight and holding in human urine for 10 hours.
[0055]The sodium acrylate 76.6g, the acrylic acid 23g, the N,N'-methylenebis acrylamide 0.4g, and 295 g of deionized water were taught to glass reaction vessels with example 1 capacity of 1 l., and the temperature of contents was kept at 5 **, stirring and mixing. The 1% solution 1g of hydrogen peroxide after it shall flow nitrogen into contents and a dissolved oxygen amount shall be 1 ppm or less, Added the 0.2% solution 1.2g and 2 of ascorbic acid, and the 2% solution 2.4g of 2'-azobis amidinopropane dihydrochloride, the polymerization was made to start, and the hydrous gel-like polymer (1) of 25% of hydrophilic resin concentration was obtained by polymerizing for about 5 hours. Kneading 400 copies of this hydrous gel-like polymer (1) by a kneader, three copies of

the 30% methanol / water mixed solutions of didecyl dimethylannmonium carbonate (methanol / water ratio = 50/50 mass %) were added, and it kneaded uniformly. After carrying out reduced pressure drying of this kneaded material at 90 ** and grinding by a pin mill, grain refining was carried out and antibacterial water absorption agent ** was obtained so that the particle size of 850-150 microns might be about 95%. The performance measurement result of this antibacterial water absorption agent ** is shown in Table 1 and 2.

[0056]In example 2 Example 1, it replaced with the 30% methanol / water mixed solution of didecyl dimethylannmonium carbonate, and antibacterial water absorption agent ** was obtained like Example 1 except using an equivalent amount of 30% methanol / water mixed solutions of didodecyl dimethylannmonium carbonate. The performance measurement result of this antibacterial water absorption agent ** is shown in Table 1 and 2.

[0057]100 copies of hydrophilic resin ("SANWETTO IM-1000" Sanyo Chemical Industries make; bridge construction thing [of a starch sodium acrylate salt copolymer]; degree % of 70 mol of neutralization) of example 3 marketing was made to absorb 400 copies of water, and the hydrous gel-like thing was obtained. Three copies of didecyl dimethylannmonium carbonate (30% methanol solution) same in this hydrous gel-like thing as Example 1 was added, grain refining was dried, ground and carried out after kneading and uniformly like Example 1 by the kneader, and antibacterial water absorption agent ** was obtained. The performance measurement result of this antibacterial water absorption agent ** is shown in Table 1 and 2.

[0058]Carrying out high speed stirring of 100 copies of hydrophilic resin ("SANWETTO IM-5800" Sanyo Chemical Industries make; surface crosslinking type hydrophilic resin which carried out surface crosslinking of the 72 mol % neutralization sodium salt of bridge construction polyacrylic acid) of example 4 marketing by a home mixer. It added little by little, 4.5 copies of the 20% methanol / water mixed solutions of didecyl dimethylannmonium carbonate (methanol / water ratio = 50/50 mass %) were mixed uniformly, and antibacterial water absorption agent ** was obtained. A mixed temperature at this time was 24 **. The performance measurement result of this antibacterial water absorption agent ** is shown in Table 1 and 2.

[0059]In example 5 Example 4, it replaced with the 20% methanol / water mixed solution of didecyl dimethylannmonium carbonate, and antibacterial water absorption agent ** was obtained like Example 4 except using an equivalent amount of 20% methanol / water mixed solutions of octyl trimethylammonium carbonate. The performance measurement result of this antibacterial water absorption agent ** is shown in Table 1 and 2.

[0060]In Example 6 and seven Examples 4, antibacterial water absorption agent ** and ** were obtained like Example 4 except replacing the addition of didecyl dimethylannmonium carbonate (20% methanol / water mixed solution) with 0.45 copy (example 6) or nine copies (example 7). The performance measurement result of these antibacterial water absorption agents is shown in Table 1 and 2.

[0061]Between two-layer pulp which is 100g/m^2, at a rate of 60 g/m^2, each basis weight sprinkled uniformly the antibacterial water absorption agent obtained in the example example 1 of an examination, and Examples 3-7, sandwiched it, and pressed it by the pressure of 5 kg/cm^2. After piling up the polyethylene film on this lower layer and piling up a polypropylene nonwoven on the upper layer, the absorbent article was created by

cutting in size of 14 cm (width) x 35 cm (length). The performance measurement result of the absorbent article (a) obtained using antibacterial water absorption agent [of Example 1] ** and antibacterial water absorption agent [of Examples 3-7] ** - **, (b), (c), (d), (e), and (f) is shown in Table 3.

[0062]After carrying out reduced pressure drying of the hydrous gel-like polymer (1) obtained in comparative example 1 Example 1 at 90 ** and grinding by a pin mill, grain refining was carried out and the comparative hydrophilic resin particulate matter <1> was obtained so that the particle size of 850-150 microns might be about 95%. The performance measurement result of <1> is shown in Table 1 and 2.

[0063]It is shown in Table 1 and 2 by making the comparative examples 2 and 3 "SANWETTO IM-1000" and the performance measurement result of "SANWETTO IM-5800" into the comparative example 2 and the comparative example 3.

[0064]In comparative example 4 Example 4, carrying out high speed stirring of 100 copies of commercial hydrophilic resin (the Sanyo Chemical Industries make, "SANWETTO IM-5800") by a home mixer, spraying addition was carried out, it mixes uniformly, nine copies of 10% solution of the benzalkonium chloride was dried, and the comparative antibacterial water absorption agent <2> was obtained. Although it was going to acquire the most uniform possible dispersion state, generation of some mass material was accepted. The performance measurement result of <2> is shown in Table 1 and 2.

[0065]In comparative example 5 Example 4, carrying out high speed stirring of 100 copies of commercial hydrophilic resin (the Sanyo Chemical Industries make, "SANWETTO IM-5800") by a home mixer. 4.5 copies of the 20% methanol / water mixed solutions of Sept Iles trimethylammonium chloride (methanol / water ratio = 50/50 mass %) were added, it mixed uniformly, and the comparative antibacterial water absorption agent <3> was obtained. The performance measurement result of <3> is shown in Table 1 and 2.

[0066]An absorbent article (g), (h), (i), (j), and (k) were obtained like the contents of the statement for the example of the example examination of a comparative study using the hydrophilic resin particulate matter or the antibacterial water absorption agent of the comparative examples 1-5. The performance measurement result of the absorbent article of these comparison is shown in Table 3.

[0067]

[Table 1]

		吸収量（g／g）	大腸菌での抗菌性（菌株数／ml）		粉体流動性（度）（g／g）
			2時間後	10時間後	
実施例	1	57	5.8×10	1.8×10	38
	2	58	2.0×10^{2}	9.5×10	39
	3	62	4.5×10	1.5×10	40
	4	58	＜5	＜5	38
	5	58	6.2×10^{2}	5.5×10^{3}	38
	6	60	2.3×10^{2}	3.3×10^{3}	37
	7	57	0	0	38
－	－	－	－	－	－
比較例	1	57	3.2×10^{8}	4.1×10^{9}	38
	2	62	4.8×10^{8}	5.4×10^{9}	40
	3	60	2.1×10^{8}	3.0×10^{9}	37
	4	51	8.5×10^{2}	7.1×10^{3}	44
	5	53	2.3×10	1.2×10	47

[0068]
[Table 2]

		アンモニア産生菌での抗菌性（菌株数／ml）		人尿中10時間後の吸収量（g／g）
		2時間後	10時間後	
実施例	1	4.9×10^{2}	2.8×10^{2}	54
	2	5.8×10^{2}	6.5×10^{2}	56
	3	2.3×10^{2}	8.4×10	58
	4	＜5	＜5	57
	5	7.8×10^{2}	9.5×10^{2}	56
	6	4.1×10^{2}	1.8×10^{3}	53
	7	0	0	57
－	－	－	－	－
比較例	1	6.3×10^{8}	5.5×10^{9}	28
	2	7.7×10^{8}	8.4×10^{9}	26
	3	7.5×10^{8}	8.3×10^{9}	34
	4	5.8×10^{4}	2.2×10^{5}	29
	5	1.6×10^{3}	3.8×10^{3}	42

[0069]
[Table 3]

吸収性物品		吸収量（ｇ／枚）	リウェット量（ｇ）	悪臭防止テスト	人尿中１０時間後の吸収量（ｇ／ｇ）
試験例	ａ	４６０	０．３	１．６	４５０
	ｂ	４９０	０．２	１．２	４８５
	ｃ	４７０	０．３	１．４	４６０
	ｄ	４７５	０．２	１．８	４７０
	ｅ	４７５	０．２	２．０	４５０
	ｆ	４７０	０．１	０．８	４７０
比較試験例	ｇ	４８５	０．３	４．４	３９０
	ｈ	４８５	０．５	４．６	３７０
	ｉ	４７５	０．４	４．１	４００
	ｊ	４６５	０．８	３．２	３９５
	ｋ	４７０	０．５	２．４	４３５

[0070]
[Effect of the Invention]The antibacterial water absorption agent of this invention has the following features and effects.
** Reveal the outstanding absorption function and the outstanding antibacterial function simultaneously. Since it excels in the antibacterial action to an ammonia production bacillus especially, generating of an ammonia smell can be prevented.
** It can control that the organic matter contained in urine, blood, body fluid, etc. which were absorbed by the water absorption agent rots by operation of fungi, a microorganism, bacteria, etc. As a result of controlling putrefaction, there is little generating of an offensive odor.
** Reveal the absorption performance stable over the long time in human urine.
** In some which only mixed conventional hydrophilic resin, adsorbing component, and deodorizing component, when both separation was produced by vibration or a shock or it applied to an absorbent article, there was a fear of hydrophilic resin, an adsorbing component, or a deodorizing component causing omnipresence within an absorbent article, but. Since the antimicrobial agent ingredient is being fixed to hydrophilic resin, the water absorption agent of this invention does not have aggravation of powder characteristics (particulate flow kinesis, dusting characteristics, etc.), and does not have worries about separation or maldistribution.
** By applying to absorbent articles, such as a disposable diaper and sanitary items, can give an antibacterial function to an absorbent article, control generating of an offensive odor, and a skin stimulus and generating of a rash decrease, and the absorption performance of an absorbent article is also good over a long time.
[0071]since the above-mentioned effect is done so, especially the antibacterial water absorption agent of this invention is useful to various absorbent articles, such as the disposable diaper for an adult and children, the pad for incontinentia persons, a sanitary

napkin, a panty liner, a breast milk pad, a mat for puerperia, and a medical-application under pad. It is useful to the gelling agent and excrement processing agent of various body fluid which generates an offensive odor by putrefaction, such as pet urine and waste blood. It is useful also when manufacturing the absorbent article of sheets shaped, such as a pet urine absorbing sheet and a drip absorber, or tape shape. In addition, a use, sludge solidifying agents (for example, a cold insulator, artificial snow, a water bed, etc.), a preventing-dew-condensation wallplate which use for hydrophilic resin the gel which made water absorb water are useful also for the use accompanied by generating of an offensive odor by putrefaction.

PRIOR ART

[Art in which an invention belongs] This invention is excellent in absorption performance, antibacterial performance, and particulate flow kinesis, and relates to an absorbent article using an antibacterial water absorption agent and this useful to an absorbent article which absorbs urine, blood, body fluid, etc. especially.
* NOTICES *

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EFFECT OF THE INVENTION

[Effect of the Invention]The antibacterial water absorption agent of this invention has the following features and effects.
** Reveal the outstanding absorption function and the outstanding antibacterial function simultaneously. Since it excels in the antibacterial action to an ammonia production bacillus especially, generating of an ammonia smell can be prevented.
** It can control that the organic matter contained in urine, blood, body fluid, etc. which were absorbed by the water absorption agent rots by operation of fungi, a microorganism, bacteria, etc. As a result of controlling putrefaction, there is little generating of an offensive odor.
** Reveal the absorption performance stable over the long time in human urine.
** In some which only mixed conventional hydrophilic resin, adsorbing component, and deodorizing component, when both separation was produced by vibration or a shock or it applied to an absorbent article, there was a fear of hydrophilic resin, an adsorbing component, or a deodorizing component causing omnipresence within an absorbent article, but. Since the antimicrobial agent ingredient is being fixed to hydrophilic resin, the water absorption agent of this invention does not have aggravation of powder characteristics (particulate flow kinesis, dusting characteristics, etc.), and does not have worries about separation or maldistribution.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]However, the constituent of these ** - ** had the problem that neither the offensive odor occurrence prevention effect not necessarily satisfying to applying to an absorbent article nor putrefaction depressor effect was acquired, or absorption performance fell by putrefaction etc. In order to satisfy an antibacterial function or a deodorizing function, post-processing of the substance which has these functions needed to be carried out to hydrophilic resin, but there was a problem that the particulate flow kinesis of the constituent obtained by this post-processing fell.

[0007]Namely, mixture ** of hydrophilic resin and zeolite, Since the hydrophilic resin and zeolite of what can adsorb to some extent and can demonstrate a deodorant effect do not have an antibacterial function, the generated offensive odor cannot control decomposition or putrefaction of a microorganism or the organic matter by fungi, and cannot prevent generating of an offensive odor. Therefore, even if applied to the absorbent article, a skin stimulus, a rash, etc. by disassembly of an organic matter were not able to be stopped. The degree of raising dust became high because zeolite separates from hydrophilic resin by vibration or a shock, and variation was looked at by the deodorizing function.

[0008]In the case of constituent ** which coated activated carbon with hydrophilic resin, and constituent ** which comprises hydrophilic resin and the deodorizing component extracted from the Theaceae vegetation. A case of the above-mentioned zeolite and same result were brought from the deodorizing component extracted from activated carbon and the Theaceae vegetation not showing an antibacterial function, and putrefaction of a microorganism or the organic matter by fungi was not able to be controlled. Since these were fixed in hydrophilic resin when using adsorbent like the zeolite of **, and the deodorizer extracted from the Theaceae vegetation of **, there was a problem of needing special operation.

[0009]Hydrophilic resin constituent ** containing a benzalkonium chloride or chlorhexidine glyconate or hydrophilic resin constituent ** containing a phosphate compound, Although a certain amount of germicidal action is accepted, the fungi which are the targets of a sterilization use, and the kind of microorganism have limitation, and satisfaction is necessarily impossible. Although the antibacterial effect over Escherichia coli or the Candida bacillus is excellent, especially a benzalkonium chloride, From a comparatively low thing, the antibacterial action to an ammonia production bacillus (Providentica rettgeri). Generating of ammonia by the organic matter in urine decomposing cannot be controlled thoroughly, but urinary pH changes with the ammonia which remains to alkalinity, and there is a problem that water absorption capacity falls as a result. The antibacterial hydrophilic resin constituent produced by processing with these antimicrobial agents had the problem that particulate flow kinesis fell depending on the throughput of an antimicrobial agent.

MEANS

[Means for Solving the Problem]This invention persons are excellent in absorption performance and particulate flow kinesis in view of the above-mentioned problem, An antibacterial action outstanding to especially an ammonia production bacillus was revealed, there was no fall of absorption performance also in the state where urine was absorbed, and this invention was reached as a result of examining a useful antibacterial water absorption agent wholeheartedly to an absorbent article used in order to absorb urine, blood, body fluid, etc.

[0011]That is, this inventions are an antibacterial water absorption agent of following [1] and [2], and an antibacterial absorbent article of [3].

[1] An antibacterial water absorption agent in which has an acid radical in a side chain and at least some acid radicals exist in a form of quarternary ammonium salt and which content of the 4th class nitrogen atom becomes from hydrophilic resin (A) which is $2x10^{-4}$ - 0.8 mass %.

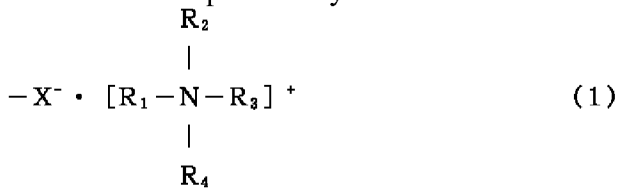
[2] An absorbed amount to ** physiological saline (0.9% sodium chloride aqueous solution) is a water absorption agent which consists of at least one sort of hydrophilic resin of 30 or more g/g, ** At least one sort of hydrophilic resin has an acid radical in a side chain, and does $2x10^{-4}$-0.8 mass % content of the 4th class nitrogen atom into ** water absorption agent ingredient, ** An antibacterial water absorption agent, wherein an absorbed amount after a viable cell equity volume measured by a mixture plate culture method after inoculating an ammonia production bacillus into a water absorption agent and cultivating for 2 hours having 1/10,000 or less antibacterial action of an early viable cell equity volume and holding in ** human urine for 10 hours is 30 or more g/g.

[3] An antibacterial absorbent article in which an antibacterial water absorption agent the above [1] or given in [2] paragraphs has the layer held in fibrous support of absorptivity.

[0012]

[Embodiment of the Invention]In the antibacterial water absorption agent [1] of this invention, hydrophilic resin (A) has an acid radical in a side chain, and at least some acid radicals exist in the form of quarternary ammonium salt. Therefore, hydrophilic resin (A) is the resin which the water absorption capacity which hydrophilic resin has, and the antibacterial performance by operation of the acid radical which exists in the form of quarternary ammonium salt had.

[0013]As a suitable example, the basis shown at the following general formula (1) is mentioned in the viewpoint of the antibacterial performance of the acid radical which exists in the form of quarternary ammonium salt in this hydrophilic resin (A).



$$-X^- \cdot [R_1-\underset{\displaystyle R_4}{\overset{\displaystyle R_2}{\underset{|}{\overset{|}{N}}}}-R_3]^+ \qquad (1)$$

X^- is the anion group which carried out the covalent bond to the polymer chain in hydrophilic resin (A) among [type, R_1 - R_4 are organic groups, and two bases chosen from R_1-R_4 may join mutually together, and they may form the ring. At least one of R_1 - R_4 is an aliphatic hydrocarbon group of the carbon numbers 5-20.]

[0014]That is, at least one of the acid radicals which carried out the covalent bond to the polymer chain in this hydrophilic resin (A) is the structure which became group X for anion $^-$ of the 4th class ammonium cation, and formed the salt. As X^-, what is necessary is just the anion group which carried out the covalent bond to the polymer chain, Although there is no restriction in particular, carboxyl anion group-COO^-, sulfonate anion group-SO_3^-, a sulphate anion group, a phosphoric acid anion group, etc. are mentioned, and desirable things are a carboxyl anion group and a sulfonate anion group, especially a carboxyl anion group. R_1, R_2, R_3, and R_4 are the viewpoints of antibacterial performance, and it is [at least one] preferably preferred a hydrocarbon group and that it is an aliphatic hydrocarbon group, especially an alkyl group more preferably, and is an alkyl group of the carbon numbers 5-20.
[0015]Hydrophilic resin (A) is a range from which the content of the 4th class nitrogen atom usually becomes $2x10^{-4}$ - 0.8 mass %, and at least some acid radicals exist in the form of quarternary ammonium salt. converting the content of the acid radical of the form of quarternary ammonium salt in this hydrophilic resin (A) into the content of the 4th class nitrogen atom to the mass of this resin -- usually -- $2x10^{-4}$ - 0.8 mass % -- desirable -- $1x10^{-3}$ - 0.4 mass % -- they are $2x10^{-3}$ - 0.1 mass % especially.

EXAMPLE

[Example]Hereafter, although an example and a comparative example explain this invention further, this invention is not limited to these. The effect check test of the absorbent article which uses the absorbed amount, the antibacterial effect, and the antibacterial water absorption agent of the antibacterial water absorption agent itself was measured by the following method. Unless the following in particular sets, % shows mass %.
[0048](1) Absorbed amount : put 1.0 g of samples into the tea bag made from a nylon net of 250 meshes, by pulling up and hanging vertically, perform a drainer for 15 minutes and measure increased weight, after dipping this into a superfluous physiological saline (0.90% salt solution) for 1 hour and making it absorb. This increased weight was made into the absorbed amount.
[0049](2) Particulate flow kinesis : evaluation of particulate flow kinesis measured the angle of repose. Measurement of an angle of repose uses a powder tester (made by Hosokawa Micron CORP.), and it is made to flow out of the tip of the glass funnels of the attachment set under the sieve on an attached disk, after it puts an adequate amount for a sample calmly in a sieve (710 micrometers of openings), carrying out vibration and tapping. When the ridgeline of the deposited granular material became a fixed angle, the protractor was moved and the angle of repose was searched for so that the outflow of a sample might be stopped and the straight part of a protractor might become parallel in the ridgeline of the deposited granular material. It means that it is inferior to particulate flow kinesis, so that an angle of repose is large.
[0050](3) The antibacterial test of an antibacterial water absorption agent : carry out autoclave sterilization after putting 3.45 g of susceptibility bouillon culture media, and 150 ml of water into a 300-cc flask and dissolving in it. After making it swell, adding and stirring 1.0 g of test samples to this culture medium, Escherichia coli (bacillus number:

JCM1649) was inoculated so that the early number of strains might serve as a $1x10^6$ individual / ml. Shaking culture of this sample is carried out at 37 **, it samples in 2 hours and 10 hours, and a sterilization isotonic sodium chloride solution performs stage dilution if needed. After putting this sampling article or 1 ml of dilution articles at a time into a sterilization petri dish, 20 ml of agar media are poured out, distributed solidification is uniformly carried out on a petri dish, and it cultivates for two days at 37 **. It is considered as a viable cell equity volume, carrying out a colony count after culture and applying dilution magnification. Viable cell equity volume measurement is performed by a mixture plate culture method. The viable cell equity volumes at the time of not adding a sample as blank on the other hand, but inoculating only Escherichia coli were a $6x10^9$ individual / ml after a $5x10^8$ individual / ml, and 10 hours after 2 hours. Antibacterial properties were similarly tested about the ammonia production bacillus. In this case, the ammonia production bacillus (Providentica rettgeri; bacillus number: IFO13501) was inoculated so that the early number of strains might serve as a $1x10^7$ individual / ml. The viable cell equity volumes at the time of not adding a sample as blank on the other hand, but inoculating only an ammonia production bacillus were a $4x10^9$ individual / ml after an $8x10^7$ individual / ml, and 10 hours after 2 hours.
[0051](4) The absorbed amount after holding in human urine for 10 hours : add 150 ml of fresh human urine (urine with which five persons' human urine was mixed), and the above-mentioned ammonia production bacillus to a 300-ml beaker, mix to it, and adjust solution temperature to 37 **. 1.0 g of samples are put into the tea bag made from a nylon net of 250 meshes, after dipping this into the above-mentioned liquid for 10 hours and absorbing and saving it, by pulling up and hanging vertically, a drainer is performed for 15 minutes and increased weight is measured. It was considered as the absorbed amount after holding this increased weight in human urine for 10 hours.
[0052](5) effect check test [of the absorbent article which applied the antibacterial water absorption agent]: -- creation [of - absorbent article]: -- put the fluff pulp layer of the tissue paper of the same size, and basis weight 100 g/m^2 on the polyethylene sheet cut out in rectangle of 14 cm x 35 cm. Subsequently, 2.94 g of samples are uniformly sprinkled on fluff pulp, and also the fluff pulp layer, the tissue paper, and the nonwoven fabric of basis weight 100 g/m^2 are piled up in this order. A model disposable diaper is created by pressing this laminated material for 90 seconds by the pressure of 5 kg/cm^2.
- Offensive odor preventive effect test : make the center section of the model disposable diaper which applied the antibacterial water absorption agent add and absorb 80 ml of fresh urine, put into a 5-l. wide mouthed bottle, and seal. This is kept for 10 hours within the thermostat set as 40 **. Then, the lid of a wide mouthed bottle is opened within an odor free room, a smell is smelled, and odour strength is evaluated in the following six steps. Evaluation is carried out by the panelist of ten bad smell decision-capabilities confirmed Mino by T&T olfactometry, and calculates average value.
[0053]
0: No odor 1 : the smell which can be perceived at last (perception IKI value concentration)
2: it understands what smell it is -- weak -- stinking (cognitive IKI value concentration)
3: smell 4: which can be perceived comfortably -- strong smell 5: -- an intense smell
[0054](6) Performance test: and the absorbed amount which is an absorbent article : the model disposable diaper was immersed for 30 minutes into the superfluous physiological

saline, and it put on the wire gauze after that, and it drained off water for 20 minutes, having applied 10 kg of load, increased weight was measured, and it was considered as the absorbed amount.
- The amount of RIWETTO : fill the center section of the model disposable diaper with 50 ml of artificial urine. Ten sheets of filter papers (10 cm x 10 cm) are put on the center section of the disposable diaper in piles in 10 minutes, and 3.5 kg of load is uniformly put from on a filter paper. The increased weight of a filter paper is measured in 3 minutes, and let this value be the amount of RIWETTO. The dry feeling of a model disposable diaper is so good that there are few amounts of RIWETTO.
The absorbed amount after holding in human urine for 10 hours : Dip a model disposable diaper for 10 hours into the 37 ** fresh human urine (urine with which five persons' human urine was mixed) which added the ammonia production bacillus, and - Absorption, It put on the wire gauze, after saving, it drained off water for 20 minutes, having applied 10 kg of load, and it was considered as the absorbed amount after measuring increased weight and holding in human urine for 10 hours.
[0055]The sodium acrylate 76.6g, the acrylic acid 23g, the N,N'-methylenebis acrylamide 0.4g, and 295 g of deionized water were taught to glass reaction vessels with example 1 capacity of 1 l., and the temperature of contents was kept at 5 **, stirring and mixing. The 1% solution 1g of hydrogen peroxide after it shall flow nitrogen into contents and a dissolved oxygen amount shall be 1 ppm or less, Added the 0.2% solution 1.2g and 2 of ascorbic acid, and the 2% solution 2.4g of 2'-azobis amidinopropane dihydrochloride, the polymerization was made to start, and the hydrous gel-like polymer (1) of 25% of hydrophilic resin concentration was obtained by polymerizing for about 5 hours. Kneading 400 copies of this hydrous gel-like polymer (1) by a kneader, three copies of the 30% methanol / water mixed solutions of didecyl dimethylannmonium carbonate (methanol / water ratio = 50/50 mass %) were added, and it kneaded uniformly. After carrying out reduced pressure drying of this kneaded material at 90 ** and grinding by a pin mill, grain refining was carried out and antibacterial water absorption agent ** was obtained so that the particle size of 850-150 microns might be about 95%. The performance measurement result of this antibacterial water absorption agent ** is shown in Table 1 and 2.
[0056]In example 2 Example 1, it replaced with the 30% methanol / water mixed solution of didecyl dimethylannmonium carbonate, and antibacterial water absorption agent ** was obtained like Example 1 except using an equivalent amount of 30% methanol / water mixed solutions of didodecyl dimethylannmonium carbonate. The performance measurement result of this antibacterial water absorption agent ** is shown in Table 1 and 2.
[0057]100 copies of hydrophilic resin ("SANWETTO IM-1000" Sanyo Chemical Industries make; bridge construction thing [of a starch sodium acrylate salt copolymer]; degree % of 70 mol of neutralization) of example 3 marketing was made to absorb 400 copies of water, and the hydrous gel-like thing was obtained. Three copies of didecyl dimethylannmonium carbonate (30% methanol solution) same in this hydrous gel-like thing as Example 1 was added, grain refining was dried, ground and carried out after kneading and uniformly like Example 1 by the kneader, and antibacterial water absorption agent ** was obtained. The performance measurement result of this antibacterial water absorption agent ** is shown in Table 1 and 2.

[0058]Carrying out high speed stirring of 100 copies of hydrophilic resin ("SANWETTO IM-5800" Sanyo Chemical Industries make; surface crosslinking type hydrophilic resin which carried out surface crosslinking of the 72 mol % neutralization sodium salt of bridge construction polyacrylic acid) of example 4 marketing by a home mixer. It added little by little, 4.5 copies of the 20% methanol / water mixed solutions of didecyl dimethylannmonium carbonate (methanol / water ratio = 50/50 mass %) were mixed uniformly, and antibacterial water absorption agent ** was obtained. A mixed temperature at this time was 24 **. The performance measurement result of this antibacterial water absorption agent ** is shown in Table 1 and 2.
[0059]In example 5 Example 4, it replaced with the 20% methanol / water mixed solution of didecyl dimethylannmonium carbonate, and antibacterial water absorption agent ** was obtained like Example 4 except using an equivalent amount of 20% methanol / water mixed solutions of octyl trimethylammonium carbonate. The performance measurement result of this antibacterial water absorption agent ** is shown in Table 1 and 2.
[0060]In Example 6 and seven Examples 4, antibacterial water absorption agent ** and ** were obtained like Example 4 except replacing the addition of didecyl dimethylannmonium carbonate (20% methanol / water mixed solution) with 0.45 copy (example 6) or nine copies (example 7). The performance measurement result of these antibacterial water absorption agents is shown in Table 1 and 2.
[0061]Between two-layer pulp which is 100g/m^2, at a rate of 60 g/m^2, each basis weight sprinkled uniformly the antibacterial water absorption agent obtained in the example example 1 of an examination, and Examples 3-7, sandwiched it, and pressed it by the pressure of 5 kg/cm^2. After piling up the polyethylene film on this lower layer and piling up a polypropylene nonwoven on the upper layer, the absorbent article was created by cutting in size of 14 cm (width) x 35 cm (length). The performance measurement result of the absorbent article (a) obtained using antibacterial water absorption agent [of Example 1] ** and antibacterial water absorption agent [of Examples 3-7] ** - **, (b), (c), (d), (e), and (f) is shown in Table 3.
[0062]After carrying out reduced pressure drying of the hydrous gel-like polymer (1) obtained in comparative example 1 Example 1 at 90 ** and grinding by a pin mill, grain refining was carried out and the comparative hydrophilic resin particulate matter <1> was obtained so that the particle size of 850-150 microns might be about 95%. The performance measurement result of <1> is shown in Table 1 and 2.
[0063]It is shown in Table 1 and 2 by making the comparative examples 2 and 3 "SANWETTO IM-1000" and the performance measurement result of "SANWETTO IM-5800" into the comparative example 2 and the comparative example 3.
[0064]In comparative example 4 Example 4, carrying out high speed stirring of 100 copies of commercial hydrophilic resin (the Sanyo Chemical Industries make, "SANWETTO IM-5800") by a home mixer, spraying addition was carried out, it mixes uniformly, nine copies of 10% solution of the benzalkonium chloride was dried, and the comparative antibacterial water absorption agent <2> was obtained. Although it was going to acquire the most uniform possible dispersion state, generation of some mass material was accepted. The performance measurement result of <2> is shown in Table 1 and 2.
[0065]In comparative example 5 Example 4, carrying out high speed stirring of 100 copies of commercial hydrophilic resin (the Sanyo Chemical Industries make,

"SANWETTO IM-5800") by a home mixer. 4.5 copies of the 20% methanol / water mixed solutions of Sept Iles trimethylammonium chloride (methanol / water ratio = 50/50 mass %) were added, it mixed uniformly, and the comparative antibacterial water absorption agent <3> was obtained. The performance measurement result of <3> is shown in Table 1 and 2.

[0066]An absorbent article (g), (h), (i), (j), and (k) were obtained like the contents of the statement for the example of the example examination of a comparative study using the hydrophilic resin particulate matter or the antibacterial water absorption agent of the comparative examples 1-5. The performance measurement result of the absorbent article of these comparison is shown in Table 3.

[0067]

[Table 1]

		吸収量	大腸菌での抗菌性（菌株数／ｍｌ）		粉体流動性
		（ｇ／ｇ）	２時間後	１０時間後	（度）（ｇ／ｇ）
実施例	1	５７	5.8×10	1.8×10	３８
	2	５８	2.0×10^{2}	9.5×10	３９
	3	６２	4.5×10	1.5×10	４０
	4	５８	＜５	＜５	３８
	5	５８	6.2×10^{2}	5.5×10^{3}	３８
	6	６０	2.3×10^{2}	3.3×10^{3}	３７
	7	５７	０	０	３８
－	－	５７	3.2×10^{8}	4.1×10^{9}	３８
比較例	1	６２	4.8×10^{8}	5.4×10^{9}	４０
	2	６０	2.1×10^{8}	3.0×10^{9}	３７
	3	５１	8.5×10^{2}	7.1×10^{3}	４４
	4	５３	2.3×10	1.2×10	４７

[0068]

[Table 2]

		アンモニア産生菌での抗菌性(菌株数／ｍｌ)		人尿中１０時間後の吸収量（ｇ／ｇ）
		２時間後	１０時間後	
実施例	1	4.9×10^{2}	2.8×10^{2}	５４
	2	5.8×10^{2}	6.5×10^{2}	５６
	3	2.3×10^{2}	8.4×10	５８
	4	＜5	＜5	５７
	5	7.8×10^{2}	9.5×10^{2}	５６
	6	4.1×10^{2}	1.8×10^{3}	５３
	7	0	0	５７
－	－	－	－	－
比較例	1	6.3×10^{8}	5.5×10^{9}	２８
	2	7.7×10^{8}	8.4×10^{9}	２６
	3	7.5×10^{8}	8.3×10^{9}	３４
	4	5.8×10^{4}	2.2×10^{5}	２９
	5	1.6×10^{3}	3.8×10^{3}	４２

[0069]
[Table 3]

吸収性物品		吸収量（ｇ／枚）	リウェット量（ｇ）	悪臭防止テスト	人尿中１０時間後の吸収量（ｇ／ｇ）
試験例	a	４６０	０．３	１．６	４５０
	b	４９０	０．２	１．２	４８５
	c	４７０	０．３	１．４	４６０
	d	４７５	０．２	１．８	４７０
	e	４７５	０．２	２．０	４５０
	f	４７０	０．１	０．８	４７０
比較試験例	g	４８５	０．３	４．４	３９０
	h	４８５	０．５	４．６	３７０
	i	４７５	０．４	４．１	４００
	j	４６５	０．８	３．２	３９５
	k	４７０	０．５	２．４	４３５

[Translation done.]